10/586274
IAP11 Rec'd PCT/PTO 18 JUL 2006

PATENT APPLICATION
CH8465
CHS 03 1 005

Metal complexes used as light-absorbent compounds in the information layer of optical data carriers

The invention relates to optical data stores comprising metal complexes in their information layer, to a process for producing them, to the metal complexes present therein, to their preparation and also to the ligands on which the metal complexes are based and processes for preparing them.

Write-once optical data carriers using specific light-absorbent substances or mixtures thereof are particularly suitable for use in high-density writable optical data stores which operate with blue laser diodes, in particular GaN or SHG laser diodes (360 – 460 nm).

The write-once compact disk (CD-R, 780 nm) has recently experienced tremendous volume growth and represents the technically established system.

The next generation of optical data stores – DVDs – is currently being introduced onto the market. The use of shorter-wavelength laser radiation (635-660 nm) and higher numerical aperture NA enables the storage density to be increased. The writable format in this case is DVD-R (DVD-R, DVD+R).

Today, optical data storage formats which use blue laser diodes (based on GaN, JP 08191171 or Second Harmonic Generation SHG JP 09050629) (360 nm - 460 nm) with high laser power are being developed. Writable optical data stores will therefore also be used in this generation. The achievable storage density depends on the focusing of the laser spot on the information plane. Spot size scales with the laser wavelength λ / NA. NA is the numerical aperture of the objective lense used. In order to obtain the highest possible storage density, the use of the smallest possible wavelength λ is the aim. At present, 390 nm is possible on the basis of semiconductor laser diodes.

The patent literature describes dye-based writable optical data stores which are equally suitable for CD-R and DVD-R systems (JP-A 11 043 481 and JP-A 10 181 206). To achieve a high reflectivity and a high modulation height of the read-out signal and also to achieve sufficient sensitivity in writing, use is made of the fact that the IR wavelength of 780 nm of CD-Rs is located at the foot of the long wavelength flank of the absorption peak of the dye and the red wavelength of 635 nm or 650 nm of DVD-Rs is located at the foot of the short wavelength flank of the absorption peak of the dye. In, for example, WO-A 09 917 284 and US-A 5 266 699, this concept is extended to the 450 nm working wavelength region on the short wavelength flank and the red and IR region on the long wavelength flank of the absorption peak.

"Express Mail" mailing label number EV848614319
Date of Deposit July 18, 2006
I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Alexandria, VA 22313-1450
Nicanor Kohncke
(Name of person mailing paper or fee)
(Signature of person mailing paper or fee)

WO-A 03/063151 likewise discloses dyes for the blue laser.

Apart from the abovementioned optical properties, the writable information layer comprising light-absorbent organic substances has to have a substantially amorphous morphology to keep the noise signal during writing or reading as small as possible. For this reason, it is particularly preferred that crystallization of the light-absorbent substances be prevented in the application of the substances by spin-coating from a solution, by vapour deposition and/or sublimation during subsequent covering with metallic or dielectric layers under reduced pressure.

The amorphous layer comprising light-absorbent substances preferably has a high heat distortion resistance, since otherwise further layers of organic or inorganic material which are applied to the light-absorbent information layer by sputtering or vapour deposition would form blurred boundaries due to diffusion and thus adversely affect the reflectivity. Furthermore, a light-absorbent substance which has insufficient heat distortion resistance can, at the boundary to a polymeric support, diffuse into the latter and once again adversely affect the reflectivity.

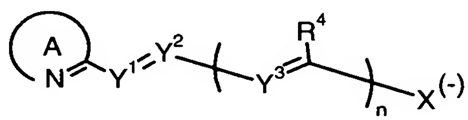
A light-absorbent substance whose vapour pressure is too high can sublime during the abovementioned deposition of further layers by sputtering or vapour deposition in a high vacuum and thus reduce the desired layer thickness. This in turn has an adverse effect on the reflectivity.

It is therefore an object of the invention to provide data carriers which comprise suitable compounds and satisfy the high requirements, e.g. light stability, favourable signal/noise ratio, damage-free application to the substrate material, and the like) for use in the information layer in a write-once optical data carrier for high-density writable optical data store formats in a laser wavelength range from 360 to 460 nm. The numerical aperture NA of the objective lense is preferably greater than or equal to 0.60, particularly preferably greater than or equal to 0.70, very particularly preferably greater than or equal to 0.80.

It has surprisingly been found that optical data carriers comprising light-absorbent compounds from the group consisting of specific metal complexes can satisfy the abovementioned requirement profile particularly well.

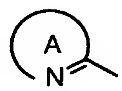
The invention accordingly provides optical data carriers comprising a preferably transparent substrate which may, if desired, have previously been coated with one or more reflection layers and/or protective layers and to whose surface a light-writable information layer, if desired one or more reflection layers and if desired a protective layer or a further substrate or a covering layer have been applied, which can be written on or read by means of blue light, preferably light having a wavelength in the range 360-460 nm, in particular from 390 to 420 nm, very particularly

preferably from 400 to 410 nm, preferably laser light, where the information layer comprises a light-absorbent compound and, if desired, a binder, characterized in that at least one metal complex having at least one ligand of the formula (I)



(I),

where

the radical of the formula  (hereinafter referred to as A for short)

is a substituted or unsubstituted and/or benzo- or naphtho-fused five- or six-membered aromatic or pseudoaromatic or partially hydrogenated heterocyclic radical,

n is 0 or 1,

Y^1 is N or C-R^1,

Y^2 is N or C-R^2,

Y^3 is N or C-R^3,

X is O, S or N-R^5,

R^5 is hydrogen, alkyl, alkenyl, aralkyl, cycloalkyl, acyl, aryl or a heterocyclic radical,

R^1 to R^4 are each, independently of one another, hydrogen, halogen, alkyl, alkoxy, monoalkylamino or dialkylamino, aralkyl, aryl, hetaryl, arylazo, hetarylazo, cyano or alkoxycarbonyl,

R^1;R^2 can form a substituted or unsubstituted triatomic bridge which may contain heteroatoms or a substituted or unsubstituted tetraatomic bridge which contains no heteroatoms or at least two heteroatoms; in particular, R^1 and R^2 together form a substituted or unsubstituted bridge having the atom sequence -CR'=N-NR"-, -(CO)-NR"-(CO)-NR'", $-(CH_2)_2-$, $-(CH_2)_3-$ or -CH=CH-CH=CH-, where R' to R'" are each, independently of one another, hydrogen, alkyl, in particular C_1-C_4-alkyl or aryl, in particular C_6-C_{10}-aryl, preferably H, methyl or phenyl,

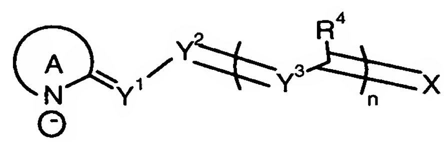
R^2;R^3 and R^4;R^5 can each, independently of one another, form a substituted or unsubstituted bridge and

R^2;R^5 can form a substituted or unsubstituted bridge when n is 0,

is used as light-absorbent compound.

n is preferably 0. Preference is likewise given to n being 1.

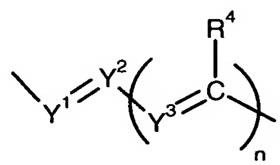
Although self-evident, it will be mentioned for the sake of completeness that ligands of the formula (I) also include the corresponding tautomers, e.g. those of the formula (I')



(I'),

where the radicals are as defined above.

In a preferred embodiment, the radical of the formula

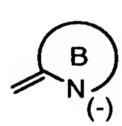


is –N=N-, -CR^1=N-, -CR^1=CR^2-, -N=CR^2-, -CR^1=N-N=CR^4-, -N=N-N=CR^4-, -CR^1=CR^2-N=CR^4- or -CR^1=CR^2-CR^3=CR^4-, particularly preferably –N=N-, -CR^1=N-, -CR^1=CR^2-, -N=CR^2-, -N=N-N=CR^4-, -CR^1=CR^2-N=CR^4- or -CR^1=CR^2-CR^3=CR^4-,

where R^1 to R^4 are as defined above.

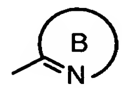
X is preferably N-R^5, where R^5 is as defined above.

Preference is likewise given to R^2 and R^5 forming a bridge when n = 0 or R^4 and R^5 forming a bridge when n = 1. In such a case,–CR^2-$N^{(-)}$-R^5 or -CR^4-$N^{(-)}$-R^5 particularly preferably form a ring of the formula (X)



(X),

with the radical of the formula (X) as the protonated tautomer of the formula



being referred to as B for short,

where B is a substituted or unsubstituted and/or benzo- or naphtho-fused 5- or 6-membered aromatic or pseudoaromatic or partially hydrogenated heterocyclic radical.

In a preferred embodiment, the metal complexes are 1:1, 1:2 or 1:3 metal complexes.

Metal complexes in which two identical or different ligands of the formula (I) are present are especially preferred.

Preference is given to metal complexes which are characterized in that they have the formula (Ia)

$$\left[(\mathrm{I})\right]_2^- \quad M^{2+} \qquad \text{(Ia)}$$

where the two ligands of the formula (I) are, independently of one another, defined as above and

M is a metal.

Preference is given to metal complexes which are characterized in that they have the formula (Ib)

$$\left[(\mathrm{I})\right]^- \quad M^{2+} \quad An^- \qquad \text{(Ib)}$$

where the ligand of the formula (I) is as defined above,

M is a metal and

An^- is an anion.

Preferred metals of the metal complexes used according to the invention are:

Mg, Ca, Sr, Ba, Cu, Ni, Co, Fe, Zn, Pd, Pt, Ru, Th, Os, Sm, B, Al, Ga, In, V, Cr, Y, La, Ce, Pr, Nd, En, Gd or Tb.

Preferred metals in the formulae (Ia) and (Ib) are divalent metals, transition metals or rare earths, in particular Mg, Ca, Sr, Ba, Cu, Ni, Co, Fe, Zn, Pd, Pt, Ru, Th, Os or Sm. Preference is given to the metals Pd, Fe, Zn, Cu, Ni and Co. Particular preference is given to Ni.

Preference is likewise given to metal complexes which are characterized in that they have the formula (Ic)

$$\left[(\mathrm{I})\right]_2^- \quad M^{3+} \quad An^- \qquad \text{(Ic)}$$

where the two ligands of the formula (I) independently have the abovementioned meanings,

M is a metal and

An^- is an anion.

Preferred metals in the formula (Ic) are trivalent metals, transition metals or rare earths, in particular B, Al, Ga, In, V, Co, Cr, Fe, Y, La, Ce, Pr, Nd, Sm, Eu, Gd or Tb. Preference is given to B, Al and Co. Particular preference is given to Co.

Preference is likewise given to random mixtures of metal complexes which are characterized in that two different ligands of the formula (I) are present in them.

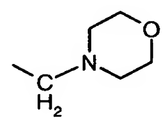
A is preferably 2-pyridyl, 2-quinolyl, 2-pyrimidyl, 2-pyrazinyl, 1,3,5-triazin-2-yl, 1,3-thiazol-2-yl, 1,3-thiazolin-2-yl, 1,3-thiazol-4-yl, benzothiazol-2-yl, 1,2-thiazol-3-yl, benzoisothiazol-3-yl, 1,3-oxazol-2-yl, 1,3-oxazolin-2-yl, benzoxazol-2-yl, 1,2-oxazol-3-yl, imidazol-2-yl, imidazolin-2-yl, benzimidazol-2-yl, imidazol-4-yl, pyrazol-5-yl, pyrrolin-2-yl, pyrrol-2-yl, 1,3,4-triazol-2-yl, 3H-indolin-2-yl, tetrahydroisoindol-1-yl, isoindol-1-yl, benz(cd)indol-2-yl, 1,3,4-thiadiazol-2-yl, 1,2,4-thiadiazol-5-yl, 1,2,4-thiadiazol-3-yl or 1,3,4-oxadiazol-2-yl, which may, if desired, be substituted.

A is particularly preferably 2-pyridyl, 2-quinolyl, 1,3-thiazol-2-yl, 1,3-thiazolin-2-yl, benzothiazol-2-yl, 1,3-oxazol-2-yl, benzoxazol-2-yl, imidazol-2-yl, benzimidazol-2-yl, pyrazol-5-yl, pyrrolin-2-yl, pyrrol-2-yl, 1,3,4-triazol-2-yl, 3H-indolin-2-yl, tetrahydroisoindol-1-yl, isoindol-1-yl, benz(cd)indol-2-yl, 1,3,4-thiadiazol-2-yl, 1,2,4-thiadiazol-5-yl or 1,3,4-oxadiazol-2-yl, which may, if desired, be substituted.

Suitable substituents for A are, for example, C_1-C_{12}-alkyl, C_1-C_{12}-alkoxy, fluorine, chlorine, bromine, iodine, hydroxy, oxo, cyano, -C(=NH)-O-C_1-C_6-alkyl, nitro, carboxy, C_1-C_6-alkoxycarbonyl, mono- or di-C_1-C_6-alkylaminocarbonyl, C_1-C_6-alkylthio, C_1-C_6-acylamino, C_1-C_6-

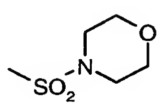
alkylsulphonylamino, C_6-C_{10}-arylsulphonylamino, formyl, C_2-C_6-alkanoyl, sulpho, mono- or di-C_1-C_6-alkylaminosulphonyl, C_6-C_{10}-aryl, C_6-C_{10}-aryloxy, C_6-C_{10}-arylcarbonylamino, mono- or di-C_1-C_6-alkylamino, N-C_1-C_6-alkyl-N-C_6-C_{10}-arylamino, pyrrolidino, morpholino, piperazino or piperidino, which may in turn be substituted if desired.

Particular preference is given to substituents from the group consisting of C_3-C_8-alkoxy radicals, for example $-O-CH_2-CH(CH_3)_2$, $-O-CH[CH(CH_3)_2]_2$, $-O-C(CH_3)_3$, $-O-CH_2-CH(C_2H_5)(C_4H_9)$, $-O-CH_2-C(CH_3)_2-C_2H_5$, branched or cyclic C_2-C_8-alkylaminomethylene radicals, for example $-CH_2N(CH_2CH(CH_3)_2)_2$, $-CH_2NH-CH_2-CH(C_2H_5)(C_4H_9)$, $-CH_2NH-CH[CH(CH_3)_2]_2$, a radical of the formula



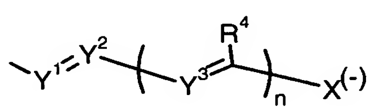
,

branched or unbranched C_2-C_5-alkoxycarbonyl radicals, for example $-COOCH_2CH_3$, $-COO-CH(CH_3)_2$, $-COO-CH[CH(CH_3)_2]_2$, branched or cyclic C_2-C_8-alkylaminosulphonyl radicals, for example $-SO_2N(CH_2CH(CH_3)_2)_2$, $-SO_2NHCH_2CH(CH_3)_2$, $-SO_2NHC(CH_3)_2CH_2CH_3$, $-SO_2NHC(CH_3)_3$, $-SO_2NH-(CH_2CH_2CH_2O-)_2CH_3$, $-SO_2NH-(CH_2CH_2CH_2O)-(CH_2CH_2O)-CH_3$, $-SO_2N(CH_2CHOH)_2$, $SO_2N(CH_2CH(CH_3)CH_2OH)_2$ and a radical of the formula



.

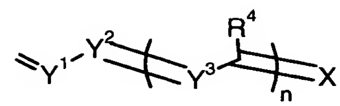
Substituents which are likewise suitable for A are, particularly in the case of A = 2-pyridyl, 1,3,4-triazol-2-yl, 1,3,4-thiadiazol-2-yl or 1,3,4-oxadiazol-2-yl, radicals of the formula (XI)



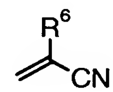
(XI),

where Y^1 to Y^3, R^4, n and X are as defined above.

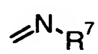
Substituents which are likewise suitable for A are, particularly in the case of A = pyrrol-2-yl in position 5 and in the case of A = tetrahydroisoindol-1-yl or isoindol-1-yl in position 3, the radical =O, =S or radicals of the formulae (XII) to (XIV)



(XII),



(XIII) or



(XIV)

where Y^1 to Y^3, R^4, n and X are as defined above but are independent thereof,

R^6 is hydrogen, C_1-C_6-alkyl or C_6-C_{10}-aryl and

R^7 is hydrogen, C_1-C_6-alkyl, C_6-C_{10}-aryl or a heterocyclic radical.

In the formulae (XI) and (XII), the radical X is preferably N-R^5, where R^5 is as defined above.

A is very particularly preferably

2-pyridyl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, ethoxy, isobutoxy, tert-butoxy, 2,4-dimethyl-3-pentoxy, diisobutylaminosulphonyl, tert-pentylaminosulphonyl, bis(hydroxyethyl)aminosulphonyl, morpholinosulphonyl, methoxyethoxypropylaminosulphonyl, nitro and cyano,

2-quinolyl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, ethoxy, isobutoxy, tert-butoxy, 2,4-dimethyl-3-pentoxy, diisobutylaminosulphonyl, tert-pentylaminosulphonyl, bis(hydroxyethyl)aminosulphonyl, morpholinosulphonyl, methoxyethoxypropylaminosulphonyl, nitro and cyano,

1,3-thiazol-2-yl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methoxy, phenyl and cyano,

benzothiazol-2-yl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, ethoxy, isobutoxy, tert-butoxy, 2,4-dimethyl-3-pentoxy, methoxycarbonyl, diisobutylaminosulphonyl, tert-pentylaminosulphonyl, bis(hydroxyethyl)aminosulphonyl, morpholinosulphonyl, methoxyethoxypropylaminosulphonyl, nitro and cyano,

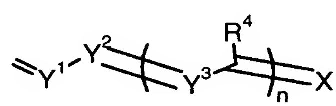
benzoxazol-2-yl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, ethoxy, isobutoxy, tert-butoxy, 2,4-dimethyl-3-pentoxy, methoxycarbonyl, diisobutylaminosulphonyl, tert-pentylaminosulphonyl, bis(hydroxyethyl)aminosulphonyl, morpholinosulphonyl, methoxyethoxypropylaminosulphonyl, nitro and cyano,

imidazol-2-yl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, methyl, methoxy, phenyl, cyano, -C(=NH)-OCH_3, nitro, methoxycarbonyl and ethoxycarbonyl,

benzimidazol-2-yl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, ethoxy, isobutoxy, tert-butoxy, 2,4-dimethyl-3-pentoxy, methoxycarbonyl, diisobutylaminosulphonyl, tert-pentylaminosulphonyl, bis(hydroxyethyl)aminosulphonyl, morpholinosulphonyl, methoxyethoxypropylaminosulphonyl, nitro and cyano,

1,3,4-thiadiazol-2-yl which may be substituted by chlorine, bromine, methoxy, phenoxy, methanesulphonyl, methylthio, ethylthio, dimethylamino, diethylamino, di(iso)propylamino, N-methyl-N-cyanoethylamino, N,N-biscyanoethylamino, N-methyl-N-hydroxyethylamino, N-methyl-N-benzylamino, N-methyl-N-phenylamino, anilino, pyrrolidino, piperidino or morpholino,

pyrrol-2-yl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, methoxycarbonyl, nitro and cyano and/or bears a -$(CH_2)_3$- or –$(CH_2)_4$ bridge in the 3,4 positions and/or can be substituted in position 5 by imino, dicyanomethylene, methoxycarbonylcyanomethylene, ethoxycarbonylcyanomethylene or a radical of the formula (XII)

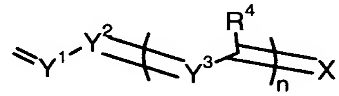


(XII),

where X is N-R^5 and Y^1 to Y^3, R^4, n and R^5 have the abovementioned meanings but are independent thereof,

3-H-indolin-2-yl which bears two methyl groups or an oxo group in position 3 and can be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, methoxycarbonyl, nitro and cyano,

isoindol-1-yl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, methoxycarbonyl, nitro and cyano and/or may be substituted in position 3 by imino, dicyanomethylene, methoxycarbonylcyanomethylene, ethoxycarbonylcyanomethylene or a radical of the formula (XII)


(XII),

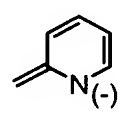
where X is N-R^5 and Y^1 to Y^3, R^4, n and R^5 have the abovementioned meanings but are independent thereof, or

1,2,4-triazol-2-yl which may be substituted by methyl or phenyl.

B as the basic structure on which the formula (X) is based preferably has the same meaning as A, but the meanings A and B are independent of one another.

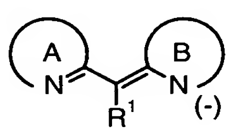
However, B is particularly preferably not substituted by a radical of the formula (XI) or (XII).

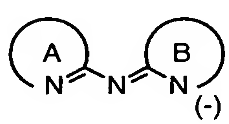
For example, when B = 2-pyridyl, B is a radical of the formula (Xa)

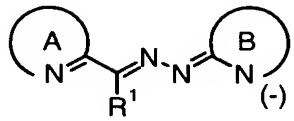

(Xa).

This applies analogously to the other heterocycles mentioned.

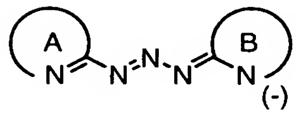
For use according to the invention, particular preference is given to metal complexes having at least one ligand of the formulae (I-A) to (I-ZA)


(I-A),

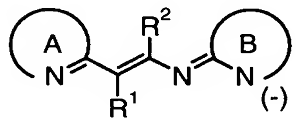

(I-B),



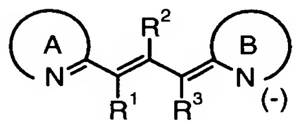
(I-C),



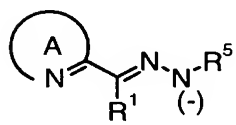
(I-D),



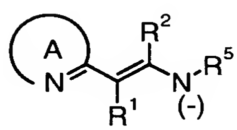
(I-E),



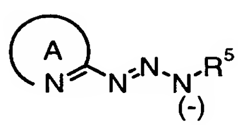
(I-F),



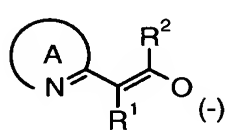
(I-G),



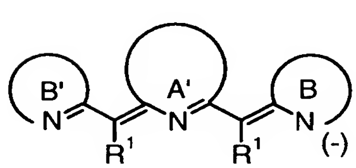
(I-H),



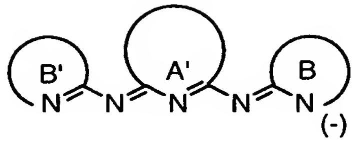
(I-I),



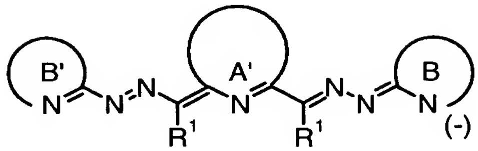
(I-J),



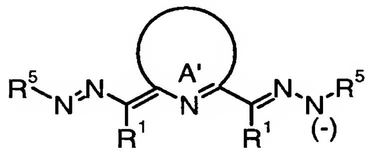
(I-K),



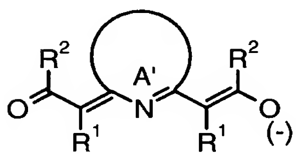
(I-L),



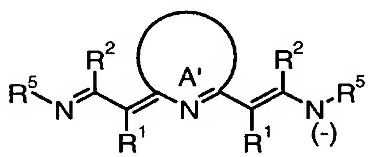
(I-M),



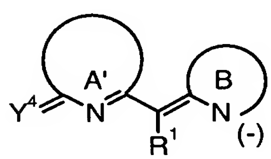
(I-N),



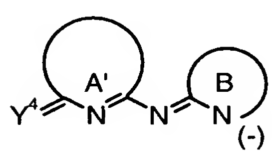
(I-O),



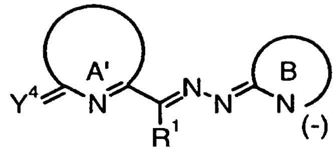
(I-P),



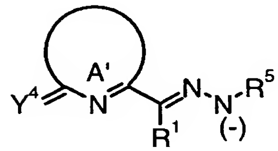
(I-Q),



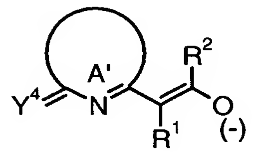
(I-R),



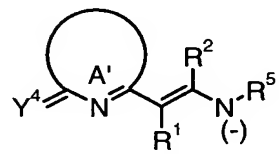
(I-S),



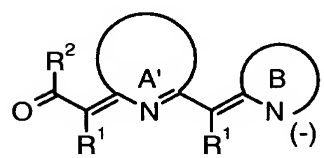
(I-T),



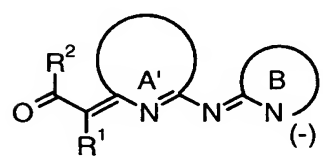
(I-U),



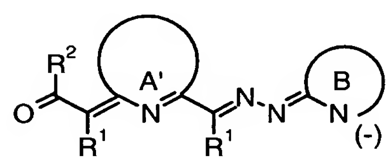
(I-V),



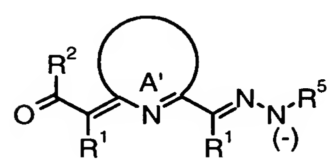
(I-W),



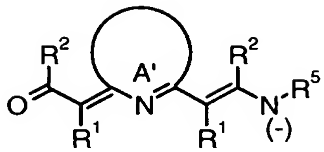
(I-X),



(I-Y),



(I-Z),



(I-ZA),

where

A and B' are, independently of one another,

2-pyridyl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, nitro and cyano,

2-quinolyl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, nitro and cyano,

1,3-thiazol-2-yl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methoxy, phenyl and cyano,

benzothiazol-2-yl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, ethoxy, isobutoxy, 2,4-dimethyl-3-pentoxy, diisobutylaminosulphonyl, methoxycarbonyl, nitro and cyano,

benzoxazol-2-yl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, ethoxy, isobutoxy, 2,4-dimethyl-3-pentoxy, diisobutylaminosulphonyl, methoxycarbonyl, nitro and cyano,

imidazol-2-yl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, methyl, methoxy, phenyl, cyano, -C(=NH)-OCH_3, nitro, methoxycarbonyl and ethoxycarbonyl,

benzimidazol-2-yl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, ethoxy, isobutoxy, 2,4-dimethyl-3-pentoxy, diisobutylaminosulphonyl, methoxycarbonyl, nitro and cyano,

1,3,4-thiadiazol-2-yl which may be substituted by chlorine, bromine, methoxy, phenoxy, methanesulphonyl, methylthio, ethylthio, dimethylamino, diethylamino, di(iso)propylamino, N-methyl-N-cyanoethylamino, N,N-biscyanoethylamino, N-methyl-N-

hydroxyethylamino, N-methyl-N-benzylamino, N-methyl-N-phenylamino, anilino, pyrrolidino, piperidino or morpholino,

3-H-indolin-2-yl which in position 3 bears two methyl groups or one oxo group and may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, methoxycarbonyl, nitro and cyano,

isoindol-1-yl which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, methoxycarbonyl, nitro and cyano and/or may be substituted in position 3 by imino, dicyanomethylene, methoxycarbonylcyanomethylene, ethoxycarbonylcyanomethylene, or

1,2,4-triazol-2-yl which may be substituted by methyl or phenyl,

A‘ is pyridin-2-yl-6-ylidene, 1,3,4-triazol-2yl-5-ylidene, pyrrol-2yl-5-ylidene, 3,4-tetramethylenepyrrol-2yl-5-ylidene or unsubstituted or fluorine-, chlorine-, methyl-, methoxy-, methoxycarbonyl-, nitro- or cyano-substituted isoindol-1-yl-3-ylidene,

B is pyridin-2-ylidene which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, nitro and cyano,

quinolin-2-ylidene which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, nitro and cyano,

1,3-thiazol-2-ylidene which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methoxy, phenyl and cyano,

benzothiazol-2-ylidene which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, ethoxy, isobutoxy, 2,4-dimethyl-3-pentoxy, diisobutylaminosulphonyl, methoxycarbonyl, nitro and cyano,

benzoxazol-2-ylidene which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, ethoxy, isobutoxy, 2,4-dimethyl-3-pentoxy, diisobutylaminosulphonyl, methoxycarbonyl, nitro and cyano,

imidazol-2-ylidene which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, methyl, methoxy, phenyl, cyano, -C(=NH)-OCH_3, nitro, methoxycarbonyl and ethoxycarbonyl,

benzimidazol-2-ylidene which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, ethoxy, isobutoxy, 2,4-dimethyl-3-pentoxy, diisobutylaminosulphonyl, methoxycarbonyl, nitro and cyano,

1,3,4-thiadiazol-2-ylidene which may be substituted by chlorine, bromine, methoxy, phenoxy, methanesulphonyl, methylthio, ethylthio, dimethylamino, diethylamino, di(iso)-propylamino, N-methyl-N-cyanoethylamino, N,N-biscyanoethylamino, N-methyl-N-hydroxyethylamino, N-methyl-N-benzylamino, N-methyl-N-phenylamino, anilino, pyrrolidino, piperidino or morpholino,

isoindol-1-ylidene which may be substituted by up to two identical or different radicals selected from the group consisting of chlorine, fluorine, methyl, methoxy, methoxycarbonyl, nitro and cyano and/or may be substituted in position 3 by imino, dicyanomethylene, methoxycarbonylcyanomethylene, ethoxycarbonylcyanomethylene, or

1,2,4-triazol-2-ylidene which may be substituted by methyl or phenyl,

R^1 to R^4 are each, independently of one another, hydrogen, chlorine, methyl, benzyl, pyridylmethyl, phenyl, cyano, methoxycarbonyl or ethoxycarbonyl and

R^2 may also be methoxy, ethoxy, dimethylamino, diethylamino, pyrrolidino or piperidino, or

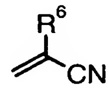
R^1;R^2 in the formulae (I-H), (I-J), (I-O), (I-P), (I-U) to (I-ZA) together form an unsubstituted or methyl-, phenyl- and/or cyano-substituted bridge having the atom sequence -CR'=N-NR"-, -(C=O)-NR"-(C=O)-NR'"-, where R' to R'" are as defined above, or

R^1;R^2 in the formulae (I-E), (I-F), (I-H), (I-J), (I-O), (I-P), (I-U) to (I-ZA) together form a -$(CH_2)_3$-, -$(CH_2)_4$- or –CH=CH-CH=CH- bridge and

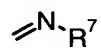
R^5 is methyl, ethyl or a phenyl, 2-, 3- or 4-pyridyl, 2-, 3- or 4-quinolyl, thiazol-2-yl, benzothiazol-2-yl, benzoxazol-2-yl, imidazol-2-yl, benzimidazol-2-yl, 1,3,4-triazol-2-yl radical which may be unsubstituted or bear up to two identical or different radicals selected from the group consisting of methyl, methoxy, chlorine, nitro, cyano, methylsulphonyl, methoxycarbonyl and ethoxycarbonyl as substituents, formyl, acetyl, trifluoroacetyl, acryloyl, methacryloyl, benzoyl, methylbenzoyl, chlorobenzoyl, methanesulphonyl, trifluoromethanesulphonyl, perfluorobutanesulphonyl, benzenesulphonyl, toluenesulphonyl, chlorobenzenesulphonyl, methoxycarbonyl, ethoxycarbonyl, N,N-dimethylcarbamoyl, N,N-dimethylsulphamoyl, N-2,2,2-

trifluoroethylsulphamoyl, N-methyl-N-2,2,2-trifluoroethylsulphamoyl, pyridine-2-, -3- or -4-carbonyl, pyridin-2-, -3- or -4-sulphonyl or benzothiazol-2-sulphonyl,

Y^4 is =O, =S or a radical of the formula



(XIII) or



(XIV),

R^6 is hydrogen, phenyl, cyano, methoxycarbonyl or ethoxycarbonyl

and

R^7 is hydrogen, methyl, ethyl, phenyl, tolyl, chlorophenyl, anisyl, 2-pyridyl, thiazol-2-yl or benzothiazol-2-yl,

where each of the formulae (I-A) to (I-ZA) is itself particularly preferred.

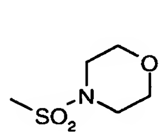
Preference is given to the formulae (I-A) to (I-C), (I-G), (I-H), (I-J) bis (I-L), (I-O), (I-Q), (I-R), (I-U), (I-W) and (I-X).

Particular preference is given to the formulae (I-A) and (I-B)

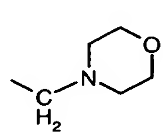
in which

R^1 is hydrogen, benzyl, phenyl, cyano, methoxycarbonyl or ethoxycarbonyl,

A is a 2-pyridyl, 1,3-thiazol-2-yl, benzothiazol-2-yl or benzoxazol-2-yl radical which is substituted by $-O-CH_2-CH(CH_3)_2$, $-O-CH[CH(CH_3)_2]_2$, $-O-C(CH_3)_3$, $-O-CH_2-CH(C_2H_5)(C_4H_9)$, $-O-CH_2-C(CH_3)_2-C_2H_5$, $-SO_2N(CH_2CH(CH_3)_2)_2$, $-COOCH_2CH_3$, $-SO_2NHCH_2CH(CH_3)_2$, $-SO_2NHC(CH_3)_2CH_2CH_3$, $-SO_2NHC(CH_3)_3$, $-CH_2N(CH_2CH(CH_3)_2)_2$, $-SO_2NH-(CH_2CH_2CH_2O-)_2CH_3$, $-SO_2NH-(CH_2CH_2CH_2O)-(CH_2CH_2O)-CH_3$, $-SO_2N(CH_2CHOH)_2$, $SO_2N(CH_2CH(CH_3)CH_2OH)_2$,

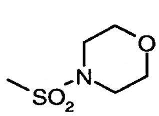


and/or

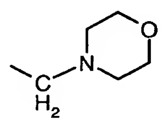


,

B is a pyridin-2-ylidene, 1,3-thiazol-2-ylidene, benzothiazol-2-ylidene or benzoxazoliden-2-yl radical which is substituted by hydrogen, $-O-CH_2-CH(CH_3)_2$, $-O-CH[CH(CH_3)_2]_2$, $-O-C(CH_3)_3$, $-O-CH_2-CH(C_2H_5)(C_4H_9)$, $-O-CH_2-C(CH_3)_2-C_2H_5$, $-SO_2N(CH_2CH(CH_3)_2)_2$, $-COOCH_2CH_3$, $-SO_2NHCH_2CH(CH_3)_2$, $-SO_2NHC(CH_3)_2CH_2CH_3$, $-SO_2NHC(CH_3)_3$, $-CH_2N(CH_2CH(CH_3)_2)_2$, $-SO_2NH-(CH_2CH_2CH_2O-)_2CH_3$, $-SO_2NH-(CH_2CH_2CH_2O)-(CH_2CH_2O)-CH_3$, $-SO_2N(CH_2CHOH)_2$, $SO_2N(CH_2CH(CH_3)CH_2OH)_2$,



and/or



.

The rings A and B in the formulae (I-A) and (I-B) very particularly preferably have the same substitution pattern.

Particular preference is given to the formula (I-C)

in which

R[1] is hydrogen, benzyl, phenyl, cyano, methoxycarbonyl or ethoxycarbonyl,

A is a 2-pyridyl, 2-quinolyl or 3,3-dimethylindolin-2-yl radical which may be substituted by methyl, methoxy, chlorine or methoxycarbonyl,

B is a pyridin-2-ylidene, 1,3-thiazol-2-ylidene or benzothiazol-2-ylidene radical which may be substituted by chlorine, methyl, methoxy, cyano or methoxycarbonyl, a 1,3,4-thiadiazol-2-ylidene radical which may be substituted by methylthio, dimethylamino, diethylamino, diisopropylamino, pyrrolidino or morpholino, or a 1,3,4-triazol-2-ylidene radical.

Very particular preference is given to the formula (I-C)

in which

R[1] is hydrogen or cyano,

A is a 2-pyridyl, 2-quinolyl or 3,3-dimethylindolin-2-yl radical,

B is a 1,3-thiazol-2-ylidene or benzothiazol-2-ylidene radical, a 1,3,4-thiadiazol-2-ylidene radical which may be substituted by dimethylamino, diethylamino, diisopropylamino, pyrrolidino or morpholino, or a 1,3,4-triazol-2-ylidene radical.

Particular preference is given to the formulae (I-G), (I-H) and (I-J)

in which

R^1 is hydrogen, phenyl or cyano,

R^2 is hydrogen or

R^1;R^2 form a -CH=CH-CH=CH- bridge,

R^5 is phenyl, tolyl, chlorophenyl, nitrophenyl, 2-, 3- or 4-pyridyl, thiazol-2-yl, benzothiazol-2-yl, trifluoroacetyl, methanesulphonyl, trifluoromethanesulphonyl, benzenesulphonyl, cyanobenzenesulphonyl, N,N-dimethylsulphamoyl, pyridine-2-, -3- or -4-sulphonyl,

A is a 2-pyridyl, 2-quinolyl or 3,3-dimethylindolin-2-yl radical which may be substituted by methyl, methoxy, chlorine or methoxycarbonyl.

Very particular preference is given to the formula (I-G)

in which

R^1 is hydrogen,

R^5 is phenyl, tolyl, chlorophenyl, nitrophenyl, 2-, 3- or 4-pyridyl, thiazol-2-yl or benzothiazol-2-yl,

A is a 2-pyridyl, 2-quinolyl or 3,3-dimethylindolin-2-yl radical which may be substituted by methyl, methoxy, chlorine or methoxycarbonyl.

Very particular preference is likewise given to the formulae (I-H) and (I-J)

in which

R^1;R^2 form a -CH=CH-CH=CH- bridge,

R^5 is trifluoroacetyl, methanesulphonyl, trifluoromethanesulphonyl, benzenesulphonyl, cyanobenzenesulphonyl, N,N-dimethylsulphamoyl, pyridine-2-, -3- or -4-sulphonyl,

A is a 2-pyridyl, 2-quinolyl or 3,3-dimethylindolin-2-yl radical which may be substituted by methyl, methoxy, chlorine or methoxycarbonyl.

Particular preference is given to the formulae (I-K) and (I-Q)

in which

R^1 is hydrogen, benzyl, phenyl, cyano, methoxycarbonyl or ethoxycarbonyl,

Y^4 is =O, =S, =NH or $=C(CN)_2$,

A‘ is 3,4-tetramethylenepyrrol-2-yl-5-ylidene, a pyrrol-2-yl-5-ylidene or isoindol-1-yl-3-ylidene radical which may be substituted by methyl, methoxy, nitro or cyano,

B‘ is a 2-pyridyl, 2-quinolyl, 1,3-thiazol-2-yl, benzothiazol-2-yl, benzoxazol-2-yl or 3,3-dimethylindolin-2-yl radical which may be substituted by methyl, methoxy, chlorine, cyano or methoxycarbonyl,

B is a pyridin-2-ylidene, quinolin-2-ylidene, 1,3-thiazol-2-ylidene, benzothiazol-2-ylidene, benzoxazol-2-ylidene or 3,3-dimethylindolin-2-ylidene radical which may be substituted by methyl, methoxy, chlorine, cyano or methoxycarbonyl.

Very particular preference is given to the formulae (I-K) and (I-Q)

in which

R^1 is hydrogen or cyano,

Y^4 is =O, =S, =NH or $=C(CN)_2$,

A‘ is a pyrrol-2-yl-5-ylidene or isoindol-1-yl-3-ylidene radical which may be substituted by methyl or methoxy,

B‘ is a 2-pyridyl, 1,3-thiazol-2-yl, benzothiazol-2-yl, benzoxazol-2-yl or 3,3-dimethylindolin-2-yl radical which may be substituted by methyl, methoxy, cyano or methoxycarbonyl,

B is a pyridin-2-ylidene, 1,3-thiazol-2-ylidene, benzothiazol-2-ylidene, benzoxazol-2-ylidene or 3,3-dimethylindolin-2-ylidene radical which may be substituted by methyl, methoxy, cyano or methoxycarbonyl, and

B and B‘ are derived from the same heterocycle.

Particular preference is given to the formulae (I-L) and (I-R)

in which

Y^4 is =O, =S, =NH or $=C(CN)_2$,

A‘ is 3,4-tetramethylenepyrrol-2-yl-5-ylidene, a pyrrol-2-yl-5-ylidene or isoindol-1-yl-3-ylidene radical which may be substituted by methyl, methoxy, nitro or cyano,

B‘ is a 2-pyridyl, 2-pyrimidyl, 1,3-thiazol-2-yl, benzothiazol-2-yl, benzoxazol-2-yl radical which may be substituted by methyl, methoxy, chlorine, cyano or methoxycarbonyl, a 1,3,4-triazol-2-yl radical or a 1,3,4-thiadiazol-2-yl radical which may be substituted by dimethylamino, diethylamino, diisopropylamino, pyrrolidino or morpholino,

B is a pyridin-2-ylidene, pyrimidin-2-ylidene, 1,3-thiazol-2-ylidene, benzothiazol-2-ylidene, benzoxazol-2-ylidene radical which may be substituted by methyl, methoxy, chlorine, cyano or methoxycarbonyl, a 1,3,4-triazol-2-ylidene radical or a 1,3,4-thiadiazol-2-ylidene radical which may be substituted by dimethylamino, diethylamino, diisopropylamino, pyrrolidono or morpholino.

Very particular preference is given to the formulae (I-L) and (I-R)

in which

Y^4 is =O, =S, =NH or $=C(CN)_2$,

A‘ is a pyrrol-2-yl-5-ylidene or isoindol-1-yl-3-ylidene radical which may be substituted by methyl or methoxy,

B‘ is a 2-pyridyl, 2-pyrimidyl, 1,3-thiazol-2-yl, benzothiazol-2-yl, benzoxazol-2-yl radical which may be substituted by methyl, methoxy or cyano, a 1,3,4-triazol-2-yl radical or a 1,3,4-thiadiazol-2-yl radical which may be substituted by dimethylamino or diisopropylamino,

B is a pyridin-2-ylidene, pyrimidin-2-ylidene, 1,3-thiazol-2-ylidene, benzothiazol-2-ylidene, benzoxazol-2-ylidene radical which may be substituted by methyl, methoxy or cyano, a 1,3,4-triazol-2-ylidene radical or a 1,3,4-thiadiazol-2-ylidene radical which may be substituted by dimethylamino or diisopropylamino, and

B and B‘ are derived from the same heterocycle.

Particular preference is given to the formulae (I-O) and (I-U)

in which

Y^4 is =O, =S, =NH or =C(CN)$_2$,

A' is 3,4-tetramethylenepyrrol-2-yl-5-ylidene, a pyrrol-2-yl-5-ylidene or isoindol-1-yl-3-ylidene radical which may be substituted by methyl, methoxy, nitro or cyano,

R^1 is hydrogen,

R^2 is methoxy, ethoxy, dimethylamino, diethylamino, pyrrolidino or piperidino or

R^1;R^2 form a –CH=CH-CH=CH- bridge.

Very particular preference is given to the formulae (I-O) and (I-U)

in which

Y^4 is =O, =S, =NH or =C(CN)$_2$,

A' is a pyrrol-2-yl-5-ylidene or isoindol-1-yl-3-ylidene radical which may be substituted by methyl or methoxy,

R^1 is hydrogen,

R^2 is dimethylamino, diethylamino, pyrrolidino or piperidino or

R^1;R^2 form a –CH=CH-CH=CH- bridge.

Particular preference is given to the formula (I-W)

in which

A' is 3,4-tetramethylenepyrrol-2-yl-5-ylidene, a pyrrol-2-yl-5-ylidene or isoindol-1-yl-3-ylidene radical which may be substituted by methyl, methoxy, nitro or cyano,

R^1 is hydrogen or cyano,

R^2 is methoxy, ethoxy, dimethylamino, diethylamino, pyrrolidino or piperidino,

B is a pyridin-2-ylidene, quinolin-2-ylidene, 1,3-thiazol-2-ylidene, benzothiazol-2-ylidene, benzoxazol-2-ylidene or 3,3-dimethylindolin-2-ylidene radical which may be substituted by methyl, methoxy, chlorine, cyano or methoxycarbonyl.

Very particular preference is given to the formula (I-W)

in which

A‘ is a pyrrol-2-yl-5-ylidene or isoindol-1-yl-3-ylidene radical which may be substituted by methyl or methoxy,

R^1 is hydrogen or cyano,

R^2 is dimethylamino, diethylamino, pyrrolidino or piperidino,

B is a pyridin-2-ylidene, 1,3-thiazol-2-ylidene, benzothiazol-2-ylidene, benzoxazol-2-ylidene or 3,3-dimethylindolin-2-ylidene radical which may be substituted by methyl, methoxy, cyano or methoxycarbonyl.

Particular preference is given to the formula (I-X)

in which

A‘ is a 3,4-tetramethylenepyrrol-2-yl-5-ylidene, pyrrol-2-yl-5-ylidene or isoindol-1-yl-3-ylidene radical which may be substituted by methyl, methoxy, nitro or cyano,

R^1 is hydrogen or cyano,

R^2 is methoxy, ethoxy, dimethylamino, diethylamino, pyrrolidino or piperidino,

B is a pyridin-2-ylidene, pyrimidin-2-ylidene, 1,3-thiazol-2-ylidene, benzothiazol-2-ylidene, benzoxazol-2-ylidene radical which may be substituted by methyl, methoxy, chlorine, cyano or methoxycarbonyl, a 1,3,4-triazol-2-ylidene radical or a 1,3,4-thiadiazol-2-ylidene radical which may be substituted by dimethylamino, diethylamino, diisopropylamino, pyrrolidino or morpholino.

Very particular preference is given to the formula (I-X)

in which

A‘ is a pyrrol-2-yl-5-ylidene or isoindol-1-yl-3-ylidene radical which may be substituted by methyl or methoxy,

R^1 is hydrogen or cyano,

R^2 is dimethylamino, diethylamino, pyrrolidino or piperidino,

B is a pyridin-2-ylidene, pyrimidin-2-ylidene, 1,3-thiazol-2-ylidene, benzothiazol-2-ylidene, benzoxazol-2-ylidene radical which may be substituted by methyl, methoxy or cyano, a 1,3,4-triazol-2-ylidene radical or a 1,3,4-thiadiazol-2-ylidene radical which may be substituted by dimethylamino or diisopropylamino.

Possible substituents for the alkyl, alkenyl or aralkyl radicals are, for the purposes of the present patent application, preferably halogen, in particular Cl or F, monoalkylamino or dialkylamino radicals, pyrrolidino, morpholino, piperidino, nitro, cyano, $CO\text{-}NH_2$, alkoxy, trialkylsilyl or trialkylsiloxy. The alkyl radicals can be linear or branched and can be partially halogenated or perhalogenated. Examples of substituted alkyl radicals are trifluoromethyl, chloroethyl, cyanoethyl, methoxyethyl. Examples of branched alkyl radicals are isopropyl, tert-butyl, 2-butyl and neopentyl.

Preferred, optionally substituted C_1-C_{12}-alkyl radicals are methyl, ethyl, n-propyl, isopropyl, n-butyl, 2-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, 2-ethylhexyl, 2,4-dimethyl-3-pentyl, 2,2-dimethylbutyl, trifluoromethyl, perfluorinated ethyl, 2,2-difluoroethyl, 3,3,3-trifluoroethyl, perfluorobutyl, cyanoethyl, methoxyethyl, chloroethyl, bisisobutylamino, bis-tert-pentylamino, morpholino. Particularly preferred, optionally substituted C_1-C_6-alkyl radicals are methyl, ethyl, n-propyl, isopropyl, n-butyl, 2-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, cyanoethyl, methoxyethyl or chloroethyl. These alkyl radicals are also present in the preferred, optionally substituted C_1-C_{12}-alkoxy radicals.

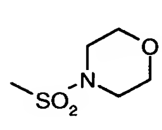
For the purposes of the present patent application, a preferred aralkyl is preferably, for example, benzyl, phenethyl or phenylpropyl.

A preferred alkenyl is, for example, allyl or 2-buten-1-yl.

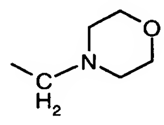
Preferred heterocyclic radicals or hetaryl radicals are pyridyl, thiazolyl, benzothiazolyl.

For the purposes of the present invention, acyl radicals are preferably formyl, C_2-C_6-alkanoyl, C_3-C_6-alkenoyl, C_6-C_{10}-aroyl, C_1-C_6-alkylsulphonyl, C_6-C_{10}-arylsulphonyl, C_1-C_6-alkoxycarbonyl, mono- or di- C_1-C_6-alkylaminocarbonyl, mono- or di- C_1-C_6-alkylaminosulphonyl or a heterocyclic radical bound via a CO or SO_2 group. Each of these acyl radicals may in turn be substituted. Examples are formyl, acetyl, trifluoroacetyl, acryloyl, methacryloyl, benzoyl, methylbenzoyl, chlorobenzoyl, methanesulphonyl, trifluoromethanesulphonyl, perfluorobutanesulphonyl,

benzenesulphonyl, toluenesulphonyl, chlorobenzenesulphonyl, methoxycarbonyl, ethoxycarbonyl, dimethylcarbamoyl, dimethylsulphamoyl, pyridine-2-, -3- or -4-carbonyl, pyridine-2-, -3- or -4-sulphonyl, benzothiazol-2-sulphonyl, pyrimidine-2-sulphonyl, $-SO_2N(CH_2CH(CH_3)_2)_2$, $-COOCH_2CH_3$, $-SO_2NHCH_2CH(CH_3)_2$, $-SO_2NHC(CH_3)_2CH_2CH_3$, $-SO_2NHC(CH_3)_3$, $-CH_2N(CH_2CH(CH_3)_2)_2$, $-SO_2NH-(CH_2CH_2CH_2O-)_2CH_3$, $-SO_2NH-(CH_2CH_2CH_2O)-(CH_2CH_2O)-CH_3$, $-SO_2N(CH_2CHOH)_2$, $SO_2N(CH_2CH(CH_3)CH_2OH)_2$,

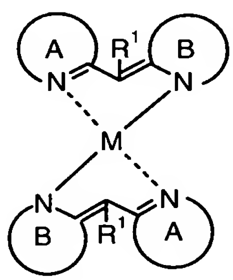


or

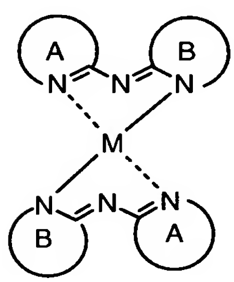


.

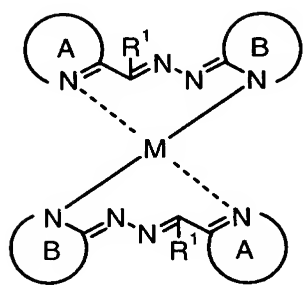
The particularly preferred metal complexes of the formula (Ia) containing ligands of the formulaes (I-A) to (I-J) and (I-Q) to (I-V) in each case have two ligands which are tautomeric forms of the formulae (II-A) to (II-K) and (II-Q) to (II-V). It is assumed that they are present in the form of the formulae (II-A) to (II-K) and (II-Q) to (II-V):

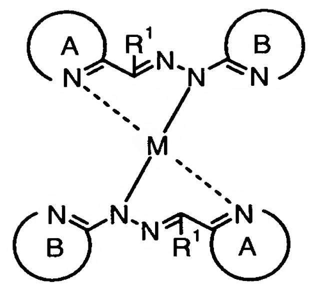


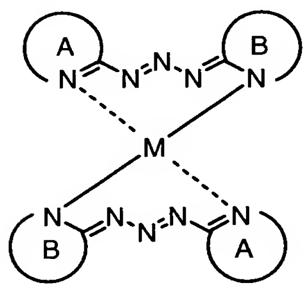
(II-A),

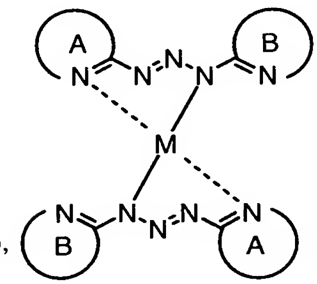


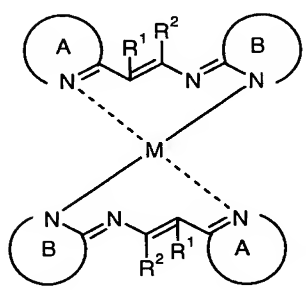
(II-B),

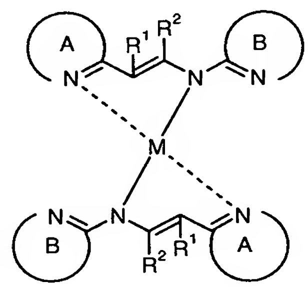

(II-Ca),

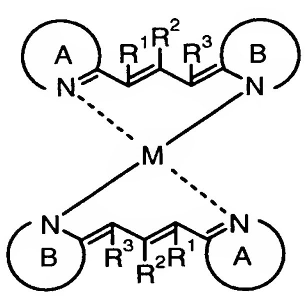

(II-Cb),

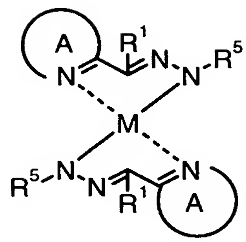

(II-Da),


(II-Db),

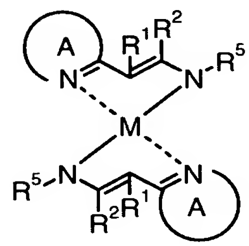

(II-Ea),


(II-Eb),

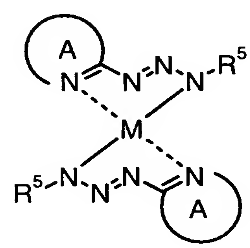

(II-F),



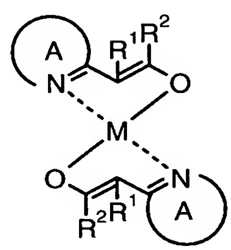
(II-G),



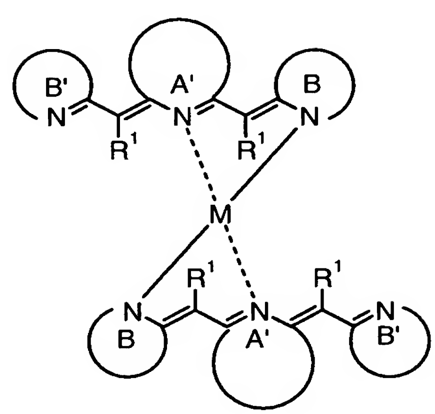
(II-H),



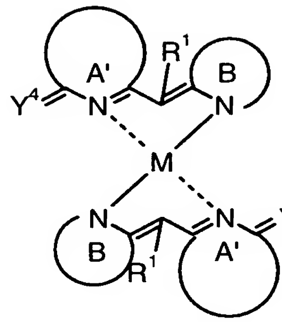
(II-I),



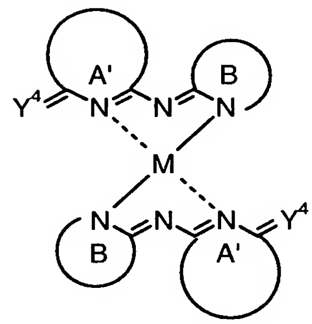
(II-J),



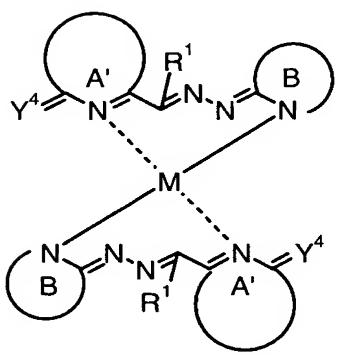
(II-K),



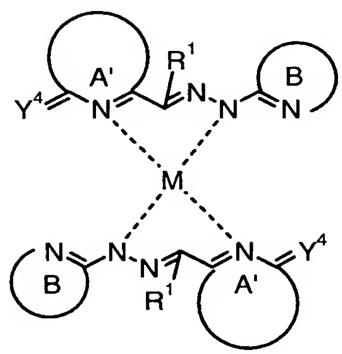
(II-Q),



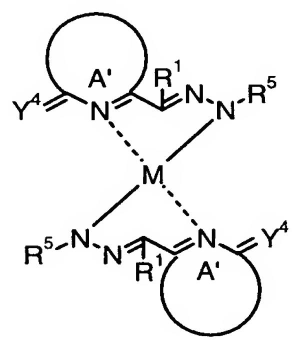
(II-R),



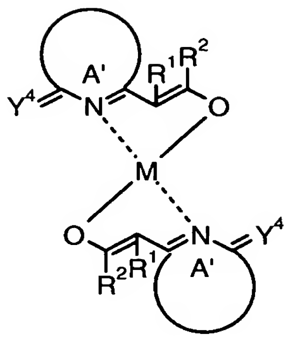
(II-Sa),



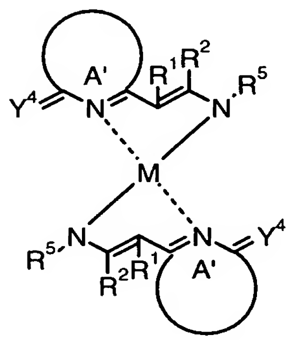
(II-Sb),



(II-T),



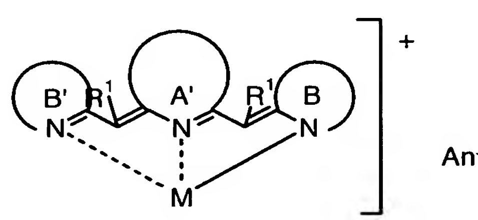
(II-U),



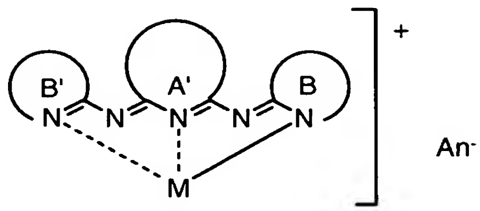
(II-V),

where M and the radicals of the respective ligands independently have the abovementioned meanings, with each of the formulae (II-A) to (II-J) and (II-Q) to (II-V) being particularly preferred themselves. For the purposes of the present patent application, it is assumed that the respective formulae (II-A) to (II-J) and (II-Q) to (II-V) are subformulae of (Ia).

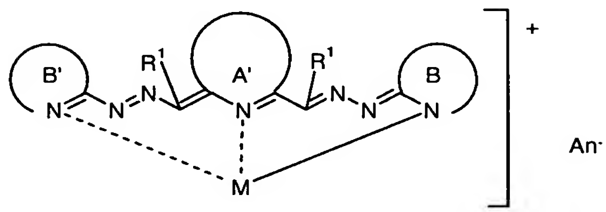
The particularly preferred metal complexes of the formula (Ib) containing ligands of the formulae (I-K) to (I-P) and (I-W) to (I-ZA) each have one ligand which is a tautomeric form of the formulae (III-K) to (III-P) and (III-W) to (III-ZA). It is assumed that they are present in the form of the formulae (III-K) to (III-P) and (III-W) to (III-ZA):



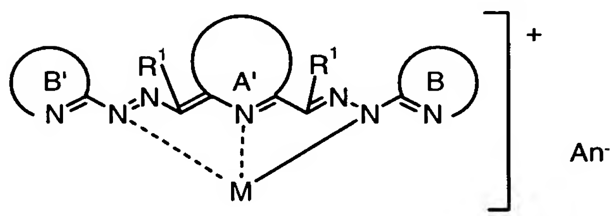
(III-K),



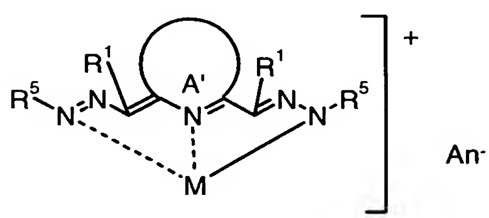
(III-L),



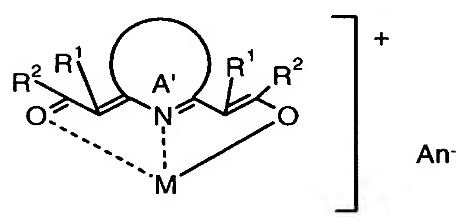
(III-Ma),



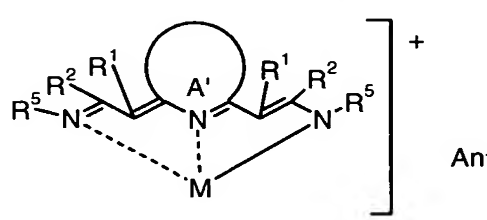
(III-Mb),



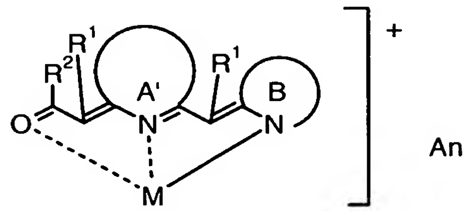
(III-N),



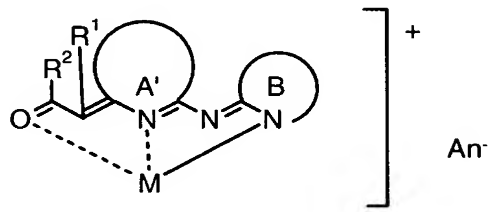
(III-O),



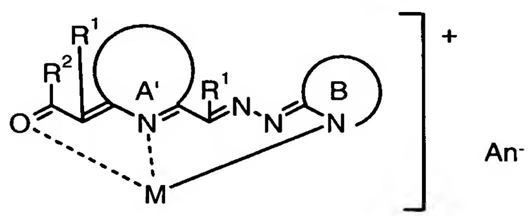
(III-P),



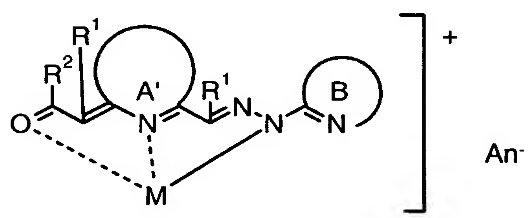
(III-W),



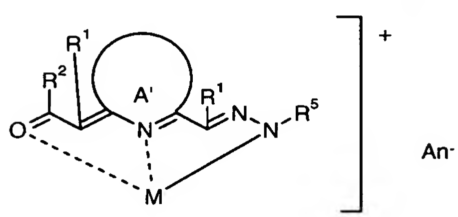
(III-X),



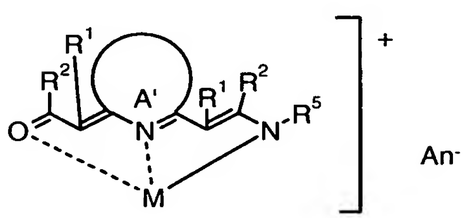
(III-Ya),



(III-Yb),



(III-Z),



(III-ZA),

where M, An^- and the radicals of the respective ligands independently have the abovementioned meanings, with each of the formulae (III-K) to (III-P) and (III-W) to (III-ZA) being particularly preferred themselves. For the purposes of the present patent application, it is assumed that the respective formulae (III-K) to (III-P) and (III-W) to (III-ZA) are subformulae of (Ib).

Possible anions An^- are all monovalent anions or an equivalent of a polyvalent anion or an equivalent of an oligomeric or polymeric anion. Preference is given to colourless anions. Suitable anions are, for example, chloride, bromide, iodide, nitrate, tetrafluoroborate, perchlorate, hexafluorosilicate, hexafluorophosphate, methosulphate, ethosulphate, C_1-C_{10}-alkanesulfonate, C_1-C_{10}-perfluoroalkanesulfonate, unsubstituted or chloro-, hydroxy-, C_1-C_4-alkoxy-substituted C_1-C_{10}-alkanoate, unsubstituted or nitro-, cyano-, hydroxy-, C_1-C_{25}-alkyl-, perfluoro-C_1-C_4-alkyl-, C_1-C_4-alkoxycarbonyl- or chloro-substituted benzenesulphonate, naphthalenesulphonate or biphenylsulphonate, unsubstituted or nitro-, cyano-, hydroxy-, C_1-C_4-alkyl-, C_1-C_4-alkoxy-, C_1-C_4-alkoxycarbonyl- or chloro-substituted benzenedisulphonate, naphthalenedisulphonate or biphenyldisulphonate, unsubstituted or nitro-, cyano-, C_1-C_4-alkyl-, C_1-C_4-alkoxy-, C_1-C_4-alkoxycarbonyl-, benzoyl-, chlorobenzoyl- or toluoyl-substituted benzoate, the anion of naphthalenedicarboxylic acid, (diphenyl ether)disulphonate, tetraphenylborate, cyanotriphenylborate, tetra-C_1-C_{20}-alkoxyborate, tetraphenoxyborate, 7,8- or 7,9-dicarba-nido-undecaborate(1-) or (2-) which may each be substituted on the B and/or C atoms by one or two C_1-C_{12}-alkyl- or phenyl groups, dodecahydrodicarbadodecaborate(2-) or B-C_1-C_{12}-alkyl-C-phenyldodecahydrodicarbadodecaborate(1-), polystyrenesulphonate, poly(meth)acrylate, polyallylsulphonate.

Preference is given to bromide, iodide, acetate, tetrafluoroborate, perchlorate, hexafluorophosphate, methanesulphonate, trifluoromethanesulphonate, benzenesulphonate, toluenesulphonate, dodecylbenzenesulphonate, tetradecanesulphonate, polystyrenesulphonate.

Furthermore, all monovalent anions or an equivalent of a polyvalent anion of a dye can be used as anions. The anionic dye An^- preferably has a similar absorption spectrum to the cationic metal complex salt. Suitable examples are anionic azo dyes, anthraquinone dyes, porphyrins, phthalocyanines, subphthalocyanines, cyanines, merocyanines, rhodamines, metal complexes, oxonols and derivatives of flavonic acid.

Very particular preference is given to metal complexes of the formula (Ia), in particular the formulae (II-A) to (II-C), (II-G), (II-H), (II-J), (II-K), (II-Q), (II-R) and (II-U),

in which

M is Pd, Fe, Zn, Cu, Ni or Co and

the other radicals have the particularly preferred and very particularly preferred meanings given above under the formulae (I-A) to (I-C), (I-G), (I-H), (I-J), (I-K), (I-Q), (I-R) and (I-U),

with each formula being very particularly preferred itself.

Very particular preference is likewise given to metal complexes of the formula (Ib), in particular the formulae (III-K), (III-L), (III-O), (III-W) and (II-X),

in which

M is Pd, Fe, Zn, Cu, Ni or Co,

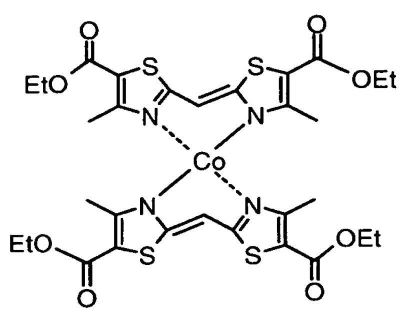
An^- is bromide, iodide, acetate, tetrafluoroborate, perchlorate, hexafluorophosphate, methanesulphonate, trifluoromethanesulphonate, benzenesulphonate, toluenesulphonate, dodecylbenzenesulphonate, tetradecanesulphonate, polystyrenesulphonate and

the other radicals have the particularly preferred and very particularly preferred meanings given above under the formulae (I-K), (I-L), (I-W) and (I-X),

with each formula being very particularly preferred itself.

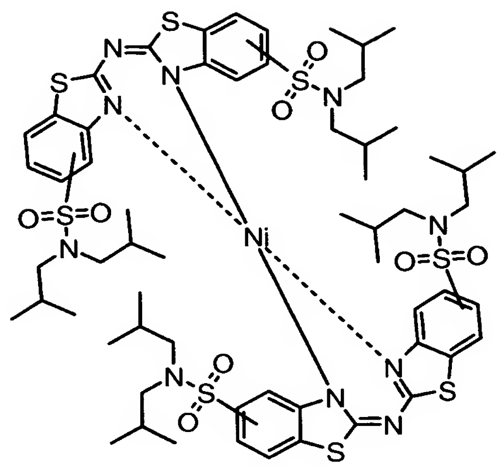
Preferred examples of metal complexes of the formulae (II-A) to (II-K) and (II-Q) to (II-V) are:

(II-A):

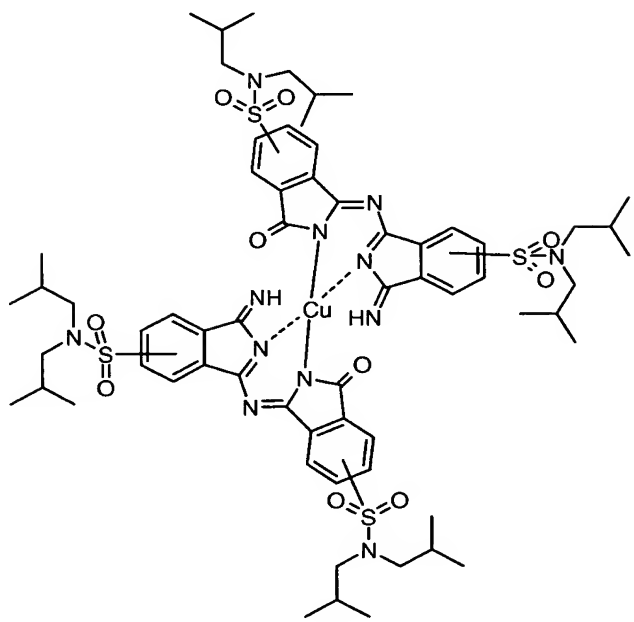


(1)

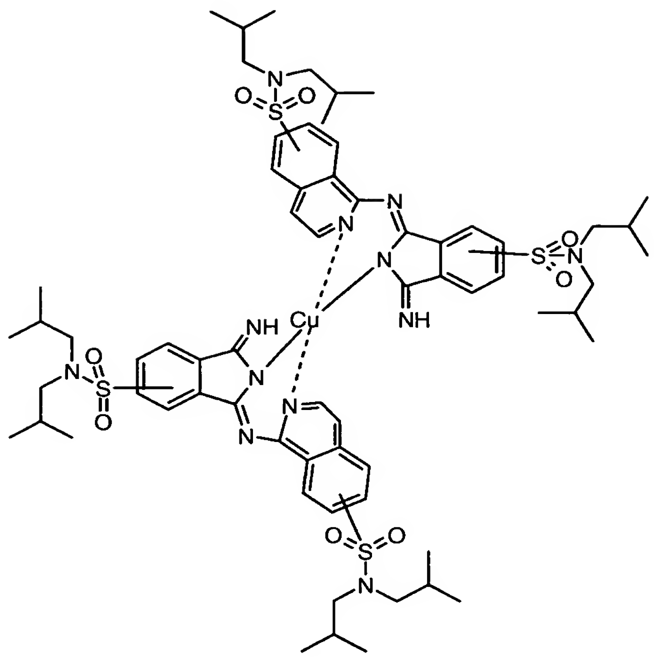
(II-B):



(1)

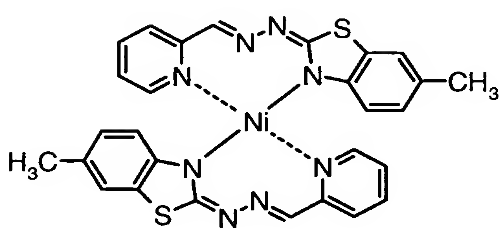


(2)



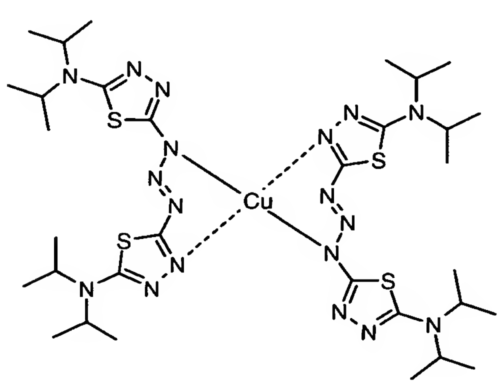
(3)

(II-C):



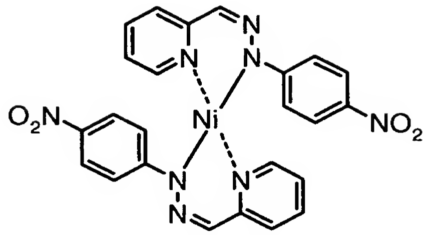
(1)

(II-D):

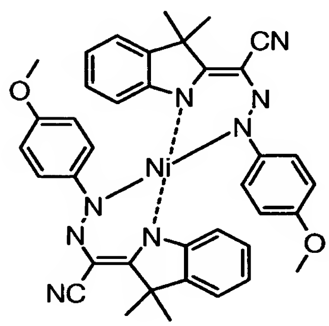


(1)

(II-G):

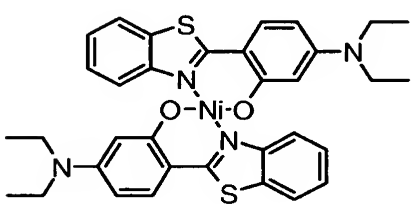


(1)

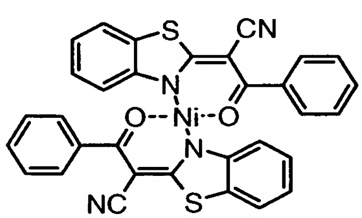


(2)

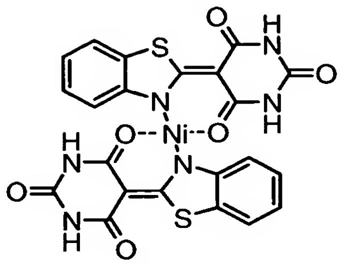
(II-J):



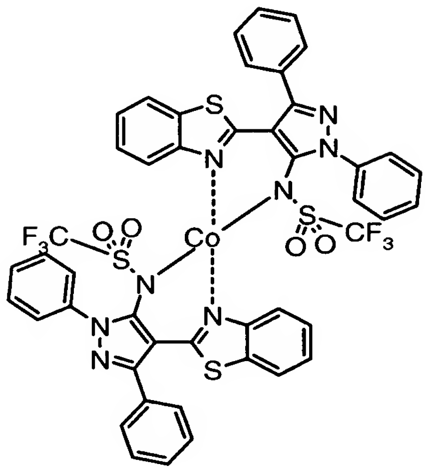
(1)



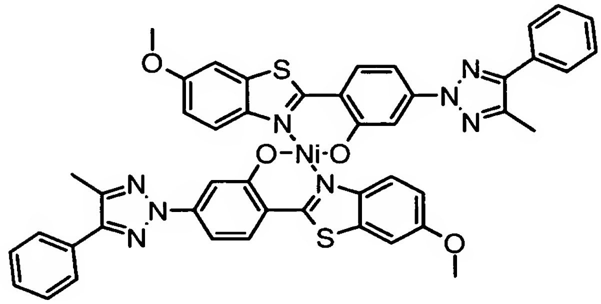
(2)



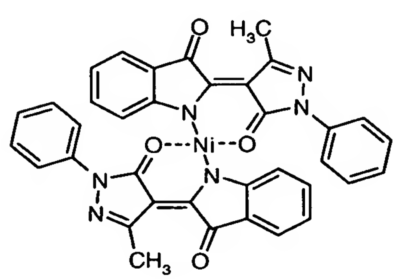
(3)



(4)

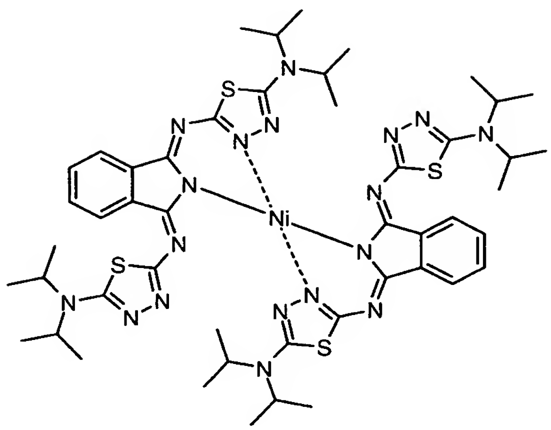


(5)

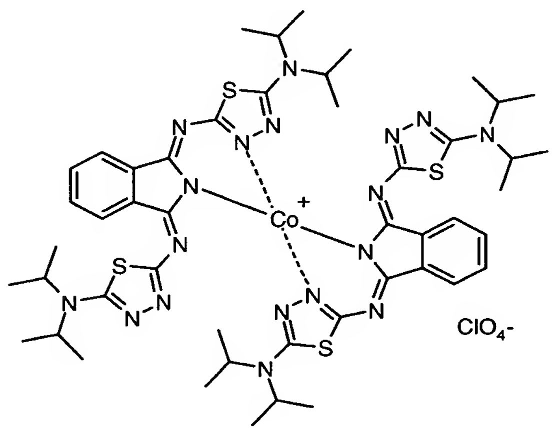


(6)

(II-K):

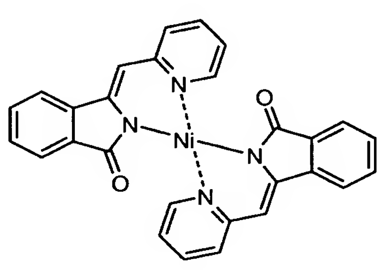


(1)

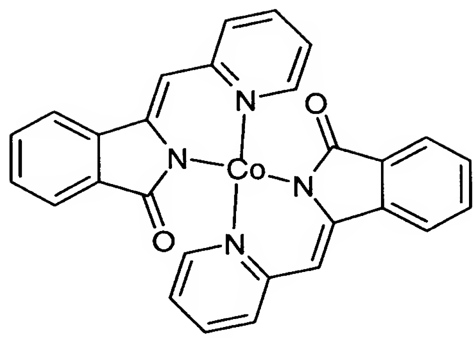


(2)

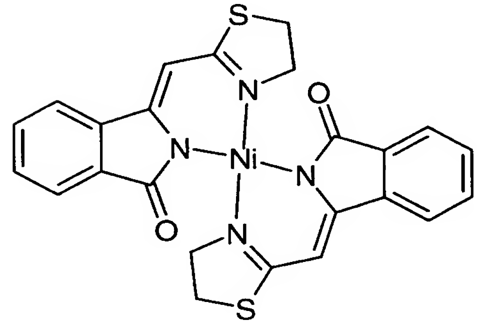
(II-Q):



(1)



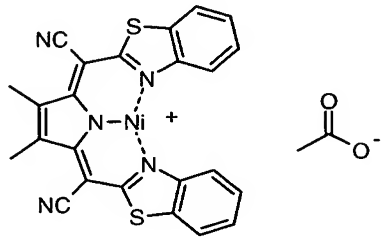
(2)



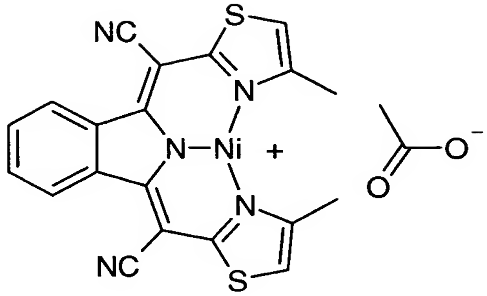
(3)

Preferred examples of metal complexes of the formulae (III-K) to (III-P) and (III-W) to (III-ZA) are:

(III-K):

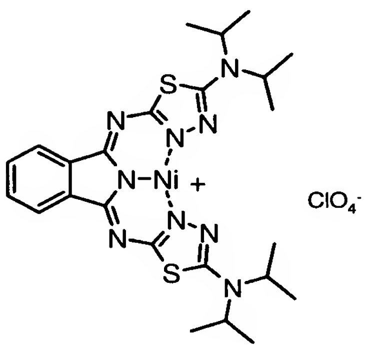


(1)

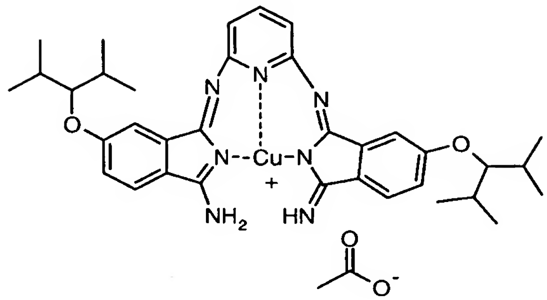


(2)

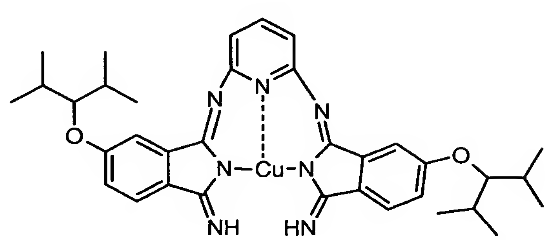
(III-L):



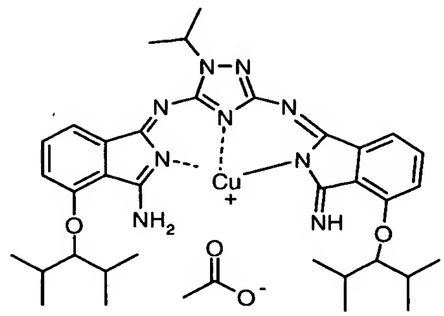
(1)



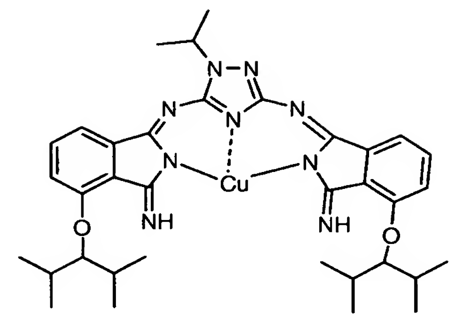
or in deprotonated form:



(2)

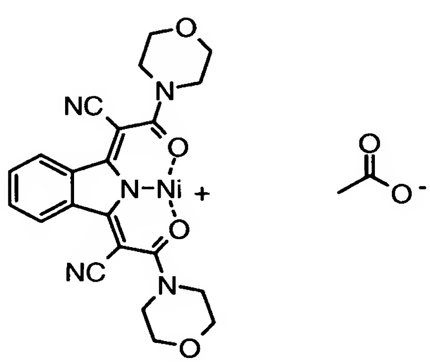


or in deprotonated form:

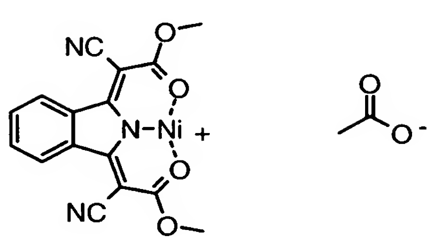


(3)

(III-O):



(1)



(2)

The light-absorbent compound should preferably be able to be changed thermally. The thermal change preferably occurs at a temperature of <600°C, particularly preferably at a temperature of <400°C, very particularly preferably at a temperature of <300°C, but at least greater than 200°C.

Such a change can be, for example, a decomposition or chemical change of the chromophoric centre of the light-absorbent compound.

In the case of the optical data carrier of the invention which is written on and read by means of light having a wavelength of from 360 to 460 nm, in particular that of a blue laser, preferred light-absorbent compounds are metal complexes whose absorption maximum λ_{max1} is in the range from 340 to 410 nm, where the wavelength $\lambda_{1/2}$ at which the absorbance in the short wavelength flank of the absorption maximum at the wavelength λ_{max1} is half of the absorbance value at λ_{max1} and the wavelength $\lambda_{1/10}$ at which the absorbance in the short wavelength flank of the absorption maximum at the wavelength λ_{max1} is one tenth of the absorbance value at λ_{max1} are preferably not more than 50 nm apart. Such a metal complex preferably has no longer-wavelength maximum λ_{max2} up to a wavelength of 500 nm, particularly preferably up to 550 nm, very particularly preferably up to 600 nm.

Preference is given to metal complexes having an absorption maximum λ_{max1} of from 345 to 400 nm, in particular from 350 to 390 nm, very particularly preferably from 360 to 380 nm.

In the case of these metal complexes, $\lambda_{1/2}$ and $\lambda_{1/10}$ as defined above are preferably not more than 40 nm apart, particularly preferably not more than 30 nm apart, very particularly preferably not more than 20 nm apart.

In the case of the optical data carrier of the invention which is written on and read by means of light having a wavelength of from 360 to 460 nm, in particular that of a blue laser, likewise preferred light-absorbent compounds are metal complexes whose absorption maximum λ_{max2} is in the range from 420 to 550 nm, where the wavelength $\lambda_{1/2}$ at which the absorbance in the short wavelength flank of the absorption maximum at the wavelength λ_{max2} is half of the absorbance value at λ_{max2} and the wavelength $\lambda_{1/10}$ at which the absorbance in the short wavelength flank of the absorption maximum at the wavelength λ_{max2} is one tenth of the absorbance value at λ_{max2} are preferably not more than 80 nm apart. Such a metal complex preferably has no shorter-wavelength maximum λ_{max1} down to a wavelength of 350 nm, particularly preferably down to 320 nm, very particularly preferably down to 290 nm.

Preference is given to metal complexes having an absorption maximum λ_{max2} of from 430 to 550 nm, in particular from 440 to 530 nm, very particularly preferably from 450 to 520 nm.

In the case of these metal complexes, $\lambda_{1/2}$ and $\lambda_{1/10}$ as defined above are preferably not more than 70 nm apart, particularly preferably not more than 50 nm apart, very particularly preferably not more than 40 nm apart.

The metal complexes have a molar extinction coefficient ε of > 30 000 l/mol cm, preferably > 50 000 l/mol cm, particularly preferably > 70 000 l/mol cm, very particularly preferably > 100 000 l/mol cm, at the absorption maximum λ_{max1} or λ_{max2}.

The absorption spectra are measured, for example, in solution.

Suitable metal complexes having the preferred spectral properties are, in particular, those which display a low solvent-induced wavelength shift (dioxane/DMF or methylene chloride/methanol). Preference is given to metal complexes whose solvent-induced wavelength shift $\Delta\lambda_{DD} = |\lambda_{DMF} - \lambda_{dioxane}|$, i.e. the positive difference between the absorption wavelengths in the solvents dimethylformamide and dioxane, or whose solvent-induced wavelength shift $\Delta\lambda_{MM} = |\lambda_{methanol} - \lambda_{methylene\ chloride}|$, i.e. the positive difference between the absorption wavelengths in the solvents methanol and methylene chloride, is <20 nm, particularly preferably < 10 nm, very particularly preferably < 5 nm.

Preference is given to an optical data carrier according to the invention which is written on and read by means of the light of a blue laser. The laser wavelength is preferably in the range from 360 to 460 nm, particularly preferably in the range from 390 to 420 nm, very particularly preferably in the range from 400 to 410 nm. The laser optics preferably has a numerical aperture NA of ≥ 0.6, particularly preferably ≥ 0.7, very particularly preferably ≥ 0.8.

Writing on and reading the optical data carrier are preferably carried out at the same wavelength.

The metal complexes used according to the invention guarantee a sufficiently high reflectivity (preferably > 10%, in particular > 20%) of the optical data carrier in the unwritten state and a sufficiently high absorption for thermal degradation of the information layer on point-wise illumination with focused light if the light wavelength is in the range from 360 to 460 nm. The contrast between written and unwritten points on the data carrier is achieved by the reflectivity change of the amplitude and also the phase of the incident light due to the changed optical properties of the information layer after thermal degradation.

The k value (imaginary part of the complex index of refraction) of the information layer comprising the metal complexes used according to the invention is preferably in the range from 0.01 to 0.40, more preferably in the range from 0.01 to 0.30, particularly preferably in the range from 0.01 to 0.20.

The n value (real part of the complex index of refraction) of the information layer comprising the metal complexes used according to the invention is preferably in the range from 0.9 to 1.3 or from

1.7 to 2.8, preferably in the range from 0.9 to 1.2 or from 1.8 to 2.8, particularly preferably in the range from 0.9 to 1.1 or from 1.9 to 2.8.

The metal complexes of the invention are preferably applied to the optical data carrier by spin coating or vacuum vapour deposition, in particular spin coating. Spin coating is carried out from solution or dispersion. The metal complexes of the invention can be mixed with one another or with other dyes having similar spectral properties. The information layer can comprise not only the metal complexes of the invention but also additives such as binders, wetting agents, stabilizers, diluents and sensitizers and also further constituents. Spin coating is preferably carried out using the above-described solutions of the metal complexes.

The information layer preferably comprises at least 70%, more preferably at least 85%, particularly preferably at least 95%, very particularly preferably 100%, of a metal complex according to the invention.

Apart from the information layer, further layers such as metal layers, dielectric layers, protective layers and covering layers may be present in the optical data store of the invention. Metals and dielectric layers serve, inter alia, to adjust the reflectivity and the heat absorption/retention. Metals can be, depending on the laser wavelength, gold, silver, aluminium, etc. Dielectric layers are, for example, silicon dioxide and silicon nitride. Protective layers and covering layers are, for example, photocurable surface coatings, (pressure-sensitive) adhesive layers and protective films.

Silicon dioxide and silicon nitride are, for example, applied by reactive sputtering. The layer thicknesses are, for example, in the range from 1 nm to 40 nm.

The metal layers are, for example, applied by sputtering. The layer thicknesses are, for example, in the range from 10 to 180 nm.

Pressure-sensitive adhesive layers consist mainly of acrylic adhesives. Nitto Denko DA-8320 or DA-8310, disclosed in the patent JP-A 11-273147, can, for example, be used for this purpose.

Protective films preferably comprise transparent material, preferably plastic films. Suitable materials are, for example, polycarbonate, copolycarbonates, PMMA and cyclic polyolefins. The thickness is, for example, from 5 to 200 μm, preferably from 10 to 180 μm, particularly preferably from 20 to 150 μm, very particularly preferably from 50 to 120 μm.

Photocurable surface coatings are, for example, UV-curable surface coatings. These are, for example, acrylates and methacrylates as are known, for example, from P. K. T. Oldring (Ed.), Chemistry & Technology of UV & EB Formulations for Coatings, Inks & Paints, Vol. 2, 1991,

SITA Technology, London, pp. 31-235. The thickness is, for example, from 5 to 200 µm, preferably from 10 to 180 µm, particularly preferably from 20 to 150 µm, very particularly preferably from 50 to 120 µm.

In addition, the optical data carrier preferably comprises at least one substrate. The substrate material is preferably transparent. Its thickness is at least 0.3 mm, preferably at least 0.6 mm and very particularly preferably at least 1.1 mm. Suitable substrate materials are preferably transparent thermoplastics or thermosets. Suitable thermoplastics are, for example, polycarbonate, copolycarbonates, PMMA and cyclic polyolefins.

The optical data carrier of the invention has, for example, the following layer structure (cf. Fig. 1): a preferably transparent substrate (1), if desired a reflection layer (7), if desired a protective layer or dielectric layer (2), an information layer (3), if desired a protective layer or dielectric layer (4), if desired an adhesive layer (5), a covering layer (6). The arrows shown in Fig. 1 and Fig. 2 indicate the path of the incident light.

The structure of the optical data carrier preferably:

comprises a preferably transparent substrate (1) to whose surface at least one light-writable information layer (3) which can be written on by means of light, preferably laser light, if desired a protective layer or dielectric layer (4), if desired an adhesive layer (5) and a transparent covering layer (6) have been applied.

comprises a preferably transparent substrate (1) to whose surface a reflection layer (7), at least one light-writable information layer (3) which can be written on by means of light, preferably laser light, if desired a protective layer or dielectric layer (4), if desired an adhesive layer (5) and a transparent covering layer (6) have been applied.

comprises a preferably transparent substrate (1) to whose surface a protective layer or dielectric layer (2), at least one information layer (3) which can be written on by means of light, preferably laser light, at least one adhesive layer (5) and a transparent covering layer (6) have been applied.

comprises a preferably transparent substrate (1) to whose surface a protective layer or dielectric layer (2), a reflection layer (7), at least one information layer (3) which can be written on by means of light, preferably laser light, if desired a protective layer or dielectric layer (4), if desired an adhesive layer (5) and a transparent covering layer (6) have been applied.

comprises a preferably transparent substrate (1) to whose surface a protective layer or dielectric layer (2) if desired, at least one information layer (3) which can be written on by means of light, preferably laser light, if desired a protective layer or dielectric layer (4), if desired an adhesive layer (5) and a transparent covering layer (6) have been applied.

comprises a preferably transparent substrate (1) to whose surface at least one information layer (3) which can be written on by means of light, preferably laser light, if desired an adhesive layer (5) and a transparent covering layer (6) have been applied.

Alternatively, the optical data carrier has, for example, the following layer structure (cf. Fig. 2): a preferably transparent substrate (11), an information layer (12) which can be written on by means of light, preferably laser light, if desired a reflection layer (13), if desired an adhesive layer (14), a further preferably transparent substrate (15).

The optical data carrier preferably contains an information layer (3) or (12).

The optical data carrier likewise preferably contains a reflection layer (7) or (13).

The optical data carrier likewise preferably contains a transparent covering layer (6).

The optical data carrier likewise preferably contains a substrate (1) or (11) or (15) comprising polycarbonate or copolycarbonate.

The substrate (1) likewise preferably has a thickness of from 0.3 to 1.5 mm, more preferably from 0.5 to 1.2 mm, in particular 1.1 mm.

The substrate (11) and (15) likewise preferably has a thickness of from 0.3 to 1.5 mm, more preferably from 0.5 to 1.2 mm, in particular 0.6 mm.

The structure of the optical data carrier is particularly preferably as follows:

a transparent substrate (1) to whose surface a reflection layer (7), an information layer (3) which can be written on and read by means of light, preferably laser light, a protective layer or dielectric layer (4), an adhesive layer (5) and a transparent covering layer (6) have been applied. The structure of the optical data carrier is likewise particularly preferably as follows:

a transparent substrate (1) to whose surface a reflection layer (7), an information layer (3) which can be written on and read by means of light, preferably laser light, a protective layer or dielectric layer (4) and a transparent covering layer (6) have been applied.

The structure of the optical data carrier is likewise particularly preferably as follows:

a transparent substrate (1) to whose surface a reflection layer (7), an information layer (3) which can be written on and read by means of light, preferably laser light, and a transparent covering layer (6) have been applied.

The structure of the optical data carrier is likewise particularly preferably as follows:

a transparent substrate (1) to whose surface a reflection layer (7), a protective layer or dielectric layer (2), an information layer (3) which can be written on and read by means of light, preferably laser light, a protective layer or dielectric layer (4), an adhesive layer (5) and a transparent covering layer (6) have been applied.

The structure of the optical data carrier is likewise particularly preferably as follows:

a transparent substrate (1) to whose surface a reflection layer (7), a protective layer or dielectric layer (2), an information layer (3) which can be written on and read by means of light, preferably laser light, a protective layer or dielectric layer (4) and a transparent covering layer (6) have been applied.

The structure of the optical data carrier is likewise particularly preferably as follows:

a transparent substrate (1) to whose surface a reflection layer (7), a protective layer or dielectric layer (2), an information layer (3) which can be written on and read by means of light, preferably laser light, and a transparent covering layer (6) have been applied.

The structure of the optical data carrier is likewise particularly preferably as follows:

a transparent substrate (1) to whose surface a protective layer or dielectric layer (2), an information layer (3) which can be written on and read by means of light, preferably laser light, a protective layer or dielectric layer (4), an adhesive layer (5) and a transparent covering layer (6) have been applied.

The structure of the optical data carrier is likewise particularly preferably as follows:

a transparent substrate (1) to whose surface a protective layer or dielectric layer (2), an information layer (3) which can be written on and read by means of light, preferably laser light, a protective layer or dielectric layer (4) and a transparent covering layer (6) have been applied.

The structure of the optical data carrier is likewise particularly preferably as follows:

a transparent substrate (1) to whose surface a protective layer or dielectric layer (2), an information layer (3) which can be written on and read by means of light, preferably laser light, and a transparent covering layer (6) have been applied.

The structure of the optical data carrier is likewise particularly preferably as follows:

a transparent substrate (11), an information layer (12) which can be written on and read by means of light, preferably laser light, a reflection layer (13), an adhesive layer (14), a further transparent substrate (15).

The invention likewise provides optical data carriers having two information layers. They can, for example, have the following structure:

a covering layer (6), if desired an adhesive layer (5), if desired a protective layer or dielectric layer (4), an information layer (3), if desired a protective layer or dielectric layer (2), if desired a reflection layer (7), a transparent substrate (1), if desired a reflection layer (7), if desired a protective layer or dielectric layer (2), an information layer (3), if desired a protective layer or dielectric layer (4), if desired an adhesive layer (5), a covering layer (6).

a preferably transparent substrate (11), an information layer (12), if desired a reflection layer (13), if desired an adhesive layer (14), if desired a protective or dielectric layer, if desired an adhesive layer (14), if desired a reflection layer (13), an information layer (12), a further preferably transparent substrate (15).

a covering layer (6), if desired an adhesive layer (5), if desired a protective layer or dielectric layer (4), an information layer (3), if desired a protective layer or dielectric layer (2), if desired a reflection layer (7), a protective layer or dielectric layer (4), an information layer (3), if desired a protective layer or dielectric layer (2), if desired a reflection layer (7), if desired a protective layer or dielectric layer (4), a transparent substrate (1).

a preferably transparent substrate (11), an information layer (12), if desired a reflection layer (13), if desired an adhesive layer (14), if desired a protective or dielectric layer, an information layer (12), if desired a reflection layer (13), a further, preferably transparent substrate (15).

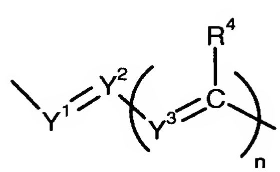
a preferably transparent substrate (11), an information layer (12), if desired a reflection layer (13), if desired a protective or dielectric layer, an information layer (12), if desired a reflection layer (13), if desired an adhesive layer (14), a further, preferably transparent substrate (15).

These optical data carriers having two information layers can also all have the abovementioned preferred layer structures in an analogous manner.

The invention further provides optical data carriers according to the invention which can be written on by means of blue light, in particular laser light.

The invention further provides a process for producing the optical data carrier of the invention, which is characterized in that a preferably transparent substrate which may, if desired, have previously been coated with a reflection layer is coated with at least one metal complex having at least one ligand of the formula (I) as light-absorbent compound, if desired in combination with suitable binders and additives and, if desired, suitable solvents and provided, if desired, with a reflection layer, further intermediate layers and, if desired, a protective layer or a further substrate or a covering layer.

The invention further provides metal complexes having at least one ligand of the formula (I) in which the radical of the formula



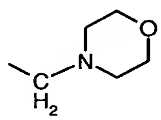
is –N=N-, $-CR^1=N-$, $-CR^1=CR^2-$, $-N=CR^2-$, $-N=N-N=CR^4-$, $-CR^1=CR^2-N=CR^4-$ or $-CR^1=CR^2-CR^3=CR^4-$,

where R^1 to R^4 and the other radicals, if they have not been specifically defined, are as defined above.

The preference ranges for the metal complexes of the invention likewise correspond to those indicated above.

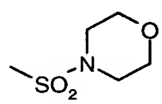
Particular preference is given to metal complexes having at least one ligand of the formula (I-A), (I-B), (I-D) to (I-L), (I-N) to (I-R), (I-T) to (I-X), (I-Z) and (I-ZA), where at least one of the rings A, A' and B in the formulae (I-A), (I-B) and (I-K) bears at least one substituent selected from the group consisting of branched C_3-C_8-alkoxy radicals, for example $-O-CH_2-CH(CH_3)_2$,

$-O-CH[CH(CH_3)_2]_2$, $-O-C(CH_3)_3$, $-O-CH_2-CH(C_2H_5)(C_4H_9)$, $-O-CH_2-C(CH_3)_2-C_2H_5$, branched or cyclic C_2-C_8-alkylaminomethylene radicals, for example $CH_2N(CH_2CH(CH_3)_2)_2$, $-CH_2NH-CH_2-CH(C_2H_5)(C_4H_9)$, $-CH_2NH-CH[CH(CH_3)_2]_2$,



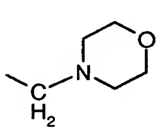
,

branched or unbranched C_2-C_5-alkoxycarbonyl radicals, for example $-COOCH_2CH_3$, $-COO-CH(CH_3)_2$, $-COO-CH[CH(CH_3)_2]_2$, unbranched, branched or cyclic C_2-C_8-alkylaminosulphonyl radicals, for example $-SO_2N(CH_2CH(CH_3)_2)_2$, $-SO_2NHCH_2CH(CH_3)_2$, $-SO_2NHC(CH_3)_2CH_2CH_3$, $-SO_2NHC(CH_3)_3$, $-SO_2NH-(CH_2CH_2CH_2O-)_2CH_3$, $-SO_2NH-(CH_2CH_2CH_2O)-(CH_2CH_2O)-CH_3$, $-SO_2N(CH_2CHOH)_2$, $SO_2N(CH_2CH(CH_3)CH_2OH)_2$,



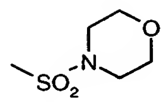
.

Particular preference is given to metal complexes of the formulae (II-A), (II-B), (II-D) to (II-K), (II-Q), (II-R), (II-T) to (II-V), (III-K), (III-L), (III-N) to (III-P), (III-W), (III-X), (III-Z) and (III-ZA), where at least one of the rings A, A' and B in the formulae (II-A), (II-B) and (III-K) bears at least one substituent selected from the group consisting of branched C_3-C_8-alkoxy radicals, for example $-O-CH_2-CH(CH_3)_2$, $-O-CH[CH(CH_3)_2]_2$, $-O-C(CH_3)_3$, $-O-CH_2-CH(C_2H_5)(C_4H_9)$, $-O-CH_2-C(CH_3)_2-C_2H_5$, branched or cyclic C_2-C_8-alkylaminomethylene radicals, for example $-CH_2N(CH_2CH(CH_3)_2)_2$, $-CH_2NH-CH_2-CH(C_2H_5)(C_4H_9)$, $-CH_2NH-CH[CH(CH_3)_2]_2$,



,

branched or unbranched C_2-C_5-alkoxycarbonyl radicals, for example $-COOCH_2CH_3$, $-COO-CH(CH_3)_2$, $-COO-CH[CH(CH_3)_2]_2$, unbranched, branched or cyclic C_2-C_8-alkylaminosulphonyl radicals, for example $-SO_2N(CH_2CH(CH_3)_2)_2$, $-SO_2NHCH_2CH(CH_3)_2$, $-SO_2NHC(CH_3)_2CH_2CH_3$, $-SO_2NHC(CH_3)_3$, $-SO_2NH-(CH_2CH_2CH_2O-)_2CH_3$, $-SO_2NH-(CH_2CH_2CH_2O)-(CH_2CH_2O)-CH_3$, $-SO_2N(CH_2CHOH)_2$, $SO_2N(CH_2CH(CH_3)CH_2OH)_2$,

.

Very particular preference is given to metal complexes of the formulae (II-D) to (II-K), (II-Q), (II-R), (II-T) to (II-V), (III-L), (III-N) to (III-P), (III-W), (III-X), (III-Z) and (III-ZA) as have been specifically given as examples above.

The metal complexes of the invention are sold, in particular, as powder or granular material or as a solution, the latter preferably having a solids content of at least 2% by weight. Preference is given to the granular form, in particular granular materials having a mean particle size of from 50 μm to 10 mm, in particular from 100 to 800 μm. Such granular materials can be produced, for example, by spray drying. The granular materials are particularly low in dust.

The metal complexes of the invention have a good solubility. They are readily soluble in nonfluorinated alcohols. Such alcohols are, for example, alcohols having from 3 to 6 carbon atoms, preferably propanol, butanol, pentanol, hexanol, diacetone alcohol or mixtures of these alcohols, e.g. propanol/diacetone alcohol, butanol/diacetone alcohol, butanol/hexanol. Preferred mixing ratios for the mixtures mentioned are, for example, from 80:20 to 99:1, preferably from 90:10 to 98:2.

Preference is likewise given to solutions comprising

a) at least one metal complex according to the invention and
b) at least one organic solvent.

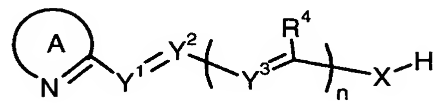
Particular preference is given to solutions comprising

a) a metal complex according to the invention and
b) an organic solvent.

The solutions preferably have a concentration of at least 1% by weight, more preferably at least 2% by weight, particularly preferably at least 5% by weight, of the metal complexes of the invention, in particular those of the formulae (Ia) to (Ic), (II-A) to (II-K), (II-Q) to (II-U) , (III-K) to (III-P) and (III-W) to (III-ZA). Solvents used are preferably 2,2,3,3-tetrafluoropropanol, propanol, butanol, pentanol, hexanol, diacetone alcohol, dibutyl ether, heptanone or mixtures thereof. Particular preference is given to 2,2,3,3-tetrafluoropropanol. Particular preference is likewise given to butanol. Butanol/diacetone alcohol in a mixing ratio of from 90:10 to 98:2 is likewise particularly preferred.

The solution particularly preferably comprises more than 95% by weight, in particular more than 98% by weight, of the components a) and b).

The invention further provides a process for preparing the metal complexes of the invention, which is characterized in that a metal salt is reacted with a ligand compound of the formula (Id)



(Id),

where

A is a substituted or unsubstituted and/or benzo- or naphtho-fused five- or six-membered aromatic or pseudoaromatic or partially hydrogenated heterocyclic radical,

n is 0 or 1,

Y^1 is N or C-R^1,

Y^2 is N or C-R^2,

Y^3 is N or C-R^3,

X is O, S or N-R^5,

R^5 is hydrogen, alkyl, alkenyl, aralkyl, cycloalkyl, acyl, aryl or a heterocyclic radical,

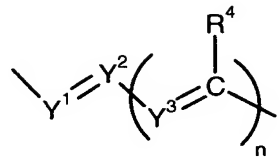
R^1 to R^4 are each, independently of one another, hydrogen, halogen, alkyl, alkoxy, monoalkylamino or dialkylamino, aralkyl, aryl, hetaryl, arylazo, hetarylazo, cyano or alkoxycarbonyl,

R^1;R^2 can form a substituted or unsubstituted triatomic bridge which may contain heteroatoms or a substituted or unsubstituted tetraatomic bridge which contains no heteroatoms or at least two heteroatoms,

R^2;R^3 and R^4;R^5 can each, independently of one another, form a bridge and

R^2;R^5 can form a bridge when n is 0,

and the radical of the formula



is –N=N-, -CR^1=N-, -CR^1=CR^1-, -N=CR^2-, -N=N-N=CR^4-, -CR^1=CR^2-N=CR^4- or -CR^1=CR^2-CR^3=CR^4-.

In this process of the invention, it is also possible to use two or more different ligand compounds of the formula (Id). This then gives a random mixture of metal complexes containing two identical ligands of the formula (I) and complexes containing two different ligands of the formula (I). These mixtures are likewise subject matter of the invention.

The reaction according to the invention is generally carried out in a solvent or solvent mixture, if appropriate in the presence of basic substances, at from room temperature to the boiling point of the solvent, for example at 20-100°C, preferably at 20-50°C. The metal complexes generally either precipitate directly and can be isolated by filtration or they are precipitated, for example, by addition of water, possibly with prior removal of part or all of the solvent, and isolated by filtration. It is also possible to carry out the reaction directly in the solvent so as to give the abovementioned concentrated solutions.

For the present purposes, metal salts are, for example, the chlorides, bromides, sulphates, hydrogensulphates, phosphates, hydrogenphosphates, dihydrogenphosphates, hydroxides, oxides, carbonates, hydrogencarbonates, carboxylates such as formates, acetates, propionates, benzoates, sulphonates such as methanesulphonates, trifluoromethanesulphonates or benzenesulphonates of the appropriate metals. For the present purposes, metal salts likewise include complexes with ligands other than those of the formula (Ia), in particular complexes of acetylacetone and of ethyl acetylacetonate. Examples of suitable metal salts are: nickel acetate, cobalt acetate, copper acetate, nickel chloride, nickel sulphate, cobalt chloride, copper chloride, copper sulphate, nickel hydroxide, nickel oxide, nickel acetylacetonate, cobalt hydroxide, basic copper carbonate, barium chloride, iron sulphate, palladium acetate, palladium chloride and their variants containing water of crystallization. Preference is given to the acetates of the metals. The metals of the metal salts employed are preferably divalent.

Examples of suitable basic substances are alkali metal acetates such as sodium acetate, potassium acetate, alkali metal hydrogencarbonates, carbonates or hydroxylates, e.g. sodium hydrogencarbonate, potassium carbonate, lithium hydroxide, sodium hydroxide, and amines such

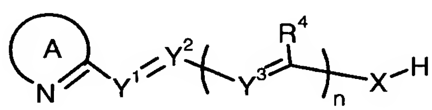
as ammonia, dimethylamine, triethylamine, diethanolamine. Such basic substances are particularly advantageous when metal salts of strong acids, e.g. the metal chlorides or sulphates, are used.

Suitable solvents are water, alcohols such as methanol, ethanol, propanol, butanol, 2,2,3,3-tetrafluoropropanol, ethers such as dibutyl ether, dioxane or tetrahydrofuran, aprotic solvents such as dimethylformamide, N-methylpyrrolidone, acetonitrile, nitromethane, dimethyl sulphoxide. Preference is given to methanol, ethanol and 2,2,3,3-tetrafluoropropanol.

The vinylic amidines and amides, hereinafter referred to as ligand compounds, of the formula (Id) required for the preparation of the metal complexes of the invention are likewise subject matter of the present invention.

The invention further provides for the use of the metal complexes of the invention as light-absorbent compounds in the information layer of write-once optical data carriers which can be written on and read by means of blue light having a wavelength in the range 360-460 nm, in particular laser light.

The invention further provides ligand compounds of the formula (Id)



(Id),

where

A is a substituted or unsubstituted and/or benzo- or naphtho-fused five- or six-membered aromatic or pseudoaromatic or partially hydrogenated heterocyclic radical,

n is 0 or 1,

Y^1 is N or C-R^1,

Y^2 is N or C-R^2,

Y^3 is N or C-R^3,

X is O, S or N-R^5,

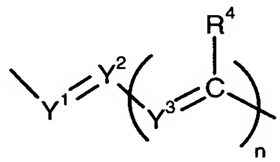
R^5 is hydrogen, alkyl, alkenyl, aralkyl, cycloalkyl, acyl, aryl or a heterocyclic radical,

R^1 to R^4 are each, independently of one another, hydrogen, halogen, alkyl, alkoxy, monoalkylamino or dialkylamino, aralkyl, aryl, hetaryl, arylazo, hetarylazo, cyano or alkoxycarbonyl,

$R^1;R^2$ can form a substituted or unsubstituted triatomic bridge which may contain heteroatoms or a substituted or unsubstituted tetraatomic bridge which contains no heteroatoms or at least two heteroatoms,

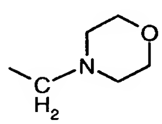
$R^2;R^3$ and $R^4;R^5$ can each, independently of one another, form a bridge and

$R^2;R^5$ can form a bridge when n is 0 and the radical of the formula



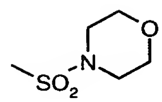
is –N=N-, $-CR^1=N-$, $-CR^1=CR^1-$, $-N=CR^2-$, $-N=N-N=CR^4-$, $-CR^1=CR^2-N=CR^4-$ or $-CR^1=CR^2-CR^3=CR^4-$.

Preferred ligand compounds correspond to the protonated form of at least one of the formulae (I-A), (I-B), (I-D) to (I-L), (I-N) to (I-R), (I-T) to (I-X), (I-Z) and (I-ZA) or a tautomeric form thereof, where at least one of the rings A and B in the formulae (I-A) and (I-B) bears at least one substituent from the group consisting of branched C_3-C_8-alkoxy radicals, for example $-O-CH_2-CH(CH_3)_2$, $-O-CH[CH(CH_3)_2]_2$, $-O-C(CH_3)_3$, $-O-CH_2-CH(C_2H_5)(C_4H_9)$, $-O-CH_2-C(CH_3)_2-C_2H_5$, branched or cyclic C_2-C_8-alkylaminomethylene radicals, for example $-CH_2N(CH_2CH(CH_3)_2)_2$, $-CH_2NH-CH_2-CH(C_2H_5)(C_4H_9)$, $-CH_2NH-CH[CH(CH_3)_2]_2$,



,

branched or unbranched C_2-C_5-alkoxycarbonyl radicals, for example $-COOCH_2CH_3$, $-COO-CH(CH_3)_2$, $-COO-CH[CH(CH_3)_2]_2$, branched or unbranched or cyclic C_2-C_8-alkylaminosulphonyl radicals, for example $-SO_2N(CH_2CH(CH_3)_2)_2$, $-SO_2NHCH_2CH(CH_3)_2$, $-SO_2NHC(CH_3)_2CH_2CH_3$, $-SO_2NHC(CH_3)_3$, $-SO_2NH-(CH_2CH_2CH_2O-)_2CH_3$, $-SO_2NH-(CH_2CH_2CH_2O)-(CH_2CH_2O)-CH_3$, $-SO_2N(CH_2CHOH)_2$, $SO_2N(CH_2CH(CH_3)CH_2OH)_2$,



Ligand compounds of the formula (Id) can be prepared by methods analogous to those given in J. Org. Chem. **2002**, *67*, 5753, Khim. Geterotsycl. Soedin. **2** (1966) 506, Pharm. Chem. J. (engl. Transl.) **7** (1973) 199, Z. Electrochem. **64** 1960) 720, Gazz. Chim. Ital. **124** (1994) 301, or C. R. Hebd. Seance Acad. Sci. **240** (1955) 983, J. Chem. Soc. Perkin Trans. II, **1984** 2111.

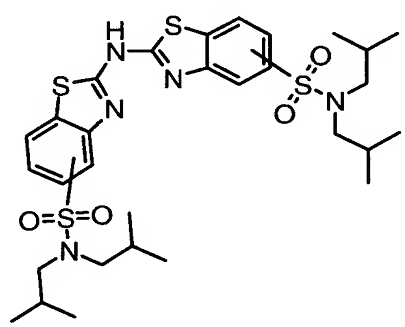
For the purposes of the present invention, all combinations of the above-disclosed general ranges and preference ranges and also the preference ranges with one another are to be considered as disclosed preference ranges.

The following examples illustrate the subject matter of the invention.

Examples

Example 1

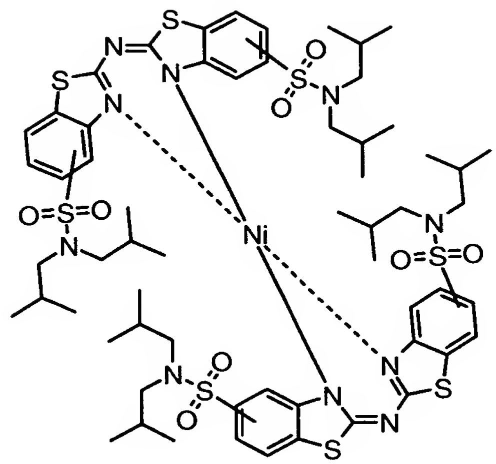
a) 5 g of bisbenzothiazol-2-ylamine were added to 20 ml of chlorosulphonic acid and the mixture was stirred overnight. 5 g of thionyl chloride were added and the mixture was stirred at 50°C for 1 hour. After cooling to room temperature, the mixture was poured onto 200 g of ice, filtered with suction and immediately stirred together with the remaining ice with 8.7 ml of diisobutylamine. After warming to room temperature, the mixture was made alkaline by means of about 0.5 ml of 50% strength by weight sodium hydroxide solution. The solid was filtered off with suction, washed with water and dried at 50°C under reduced pressure. This gave 11.1 g (95% of theory) of a yellow powder having the formula



MS: m/e = 665

UV (CH_2Cl_2): λ_{max} = 359, 376 nm.

b) 2.48 g of the product from a) was stirred overnight with 1.25 g of nickel acetate tetrahydrate in 20 ml at room temperature. The solid was then filtered off with suction, washed with methanol and water and dried at 50°C under reduced pressure. This gave 1.8 g (70% of theory) of a beige powder having the formula



Mp. = 173-175°C

MS: m/e = 1388

UV (CH_2Cl_2): λ_{max} = 365, 376 nm.

A 2% strength by weight solution in TFP (2,2,3,3-tetrafluoropropanol) applied to a glass plate gives a glass-like transparent film.

Example 1a

The corresponding cobalt complex was able to be prepared in an analogous way.

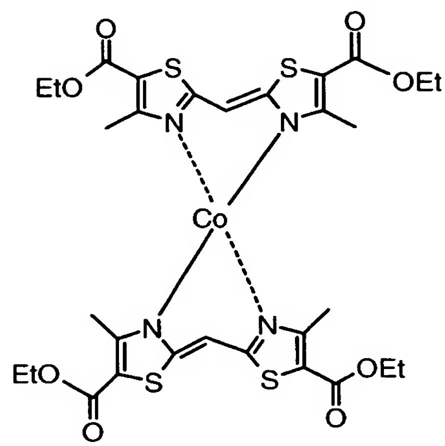
Mp. = 238-240°C

MS: m/e = 1387

UV (CH_2Cl_2): λ_{max} = 363, 378 nm.

Example 1b

5 g of bis(4-methyl-5-ethoxycarbonylthiazol-2-yl)methane were stirred with 1.8 g of cobalt acetate tetrahydrate in 20 ml of ethanol at 60°C for 4 hours. After cooling, the solid was filtered off with suction, washed with ethanol and water and dried at 50°C under reduced pressure. This gave 5.0 g (93% of theory) of a yellow powder having the formula

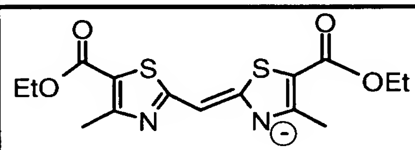
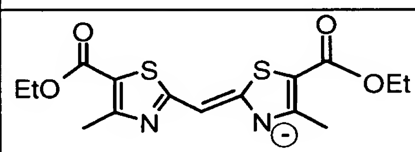
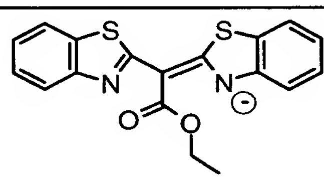


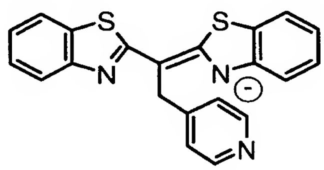
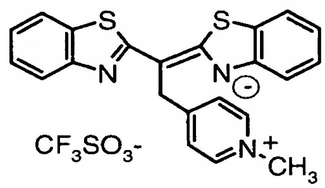
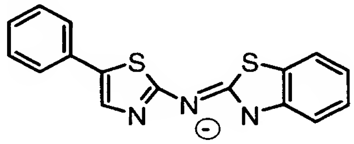
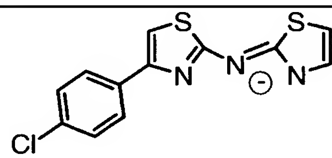
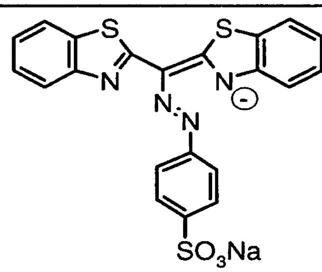
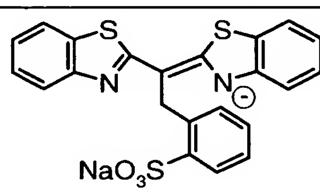
MS: m/e = 765

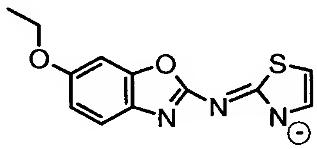
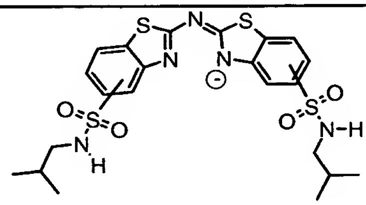
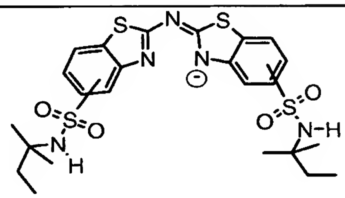
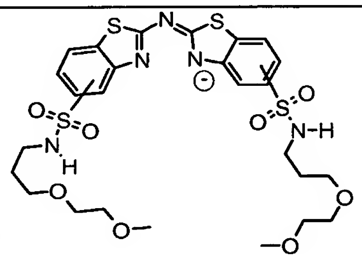
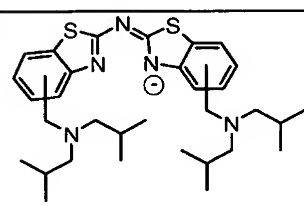
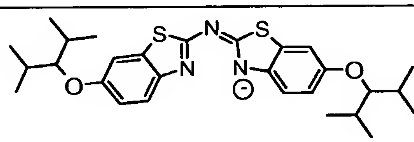
UV (CH_2Cl_2): λ_{max} = 455 nm.

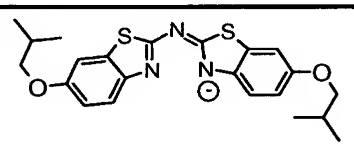
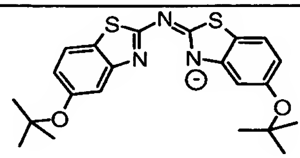
The examples in the following table were also prepared by methods analogous to the above examples.

Table 1

Example	(I)	M	λ_{max}
1c		Ni	
1d		Zn	464 nm
1e		Ni	373, 387 nm

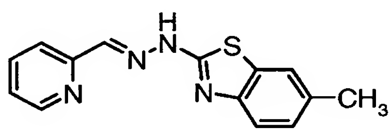
Example	(I)	M	λ_{max}
1f		Co	
1g		Ni	
1h		Zn	
1i		Ni	
1j		Ni	
1k		Cu	

Example	(I)	M	λ_{max}
1l		Ni	
1m		Pd	
1n		Ni	
1o		Co	
1p		Ni	
1q		Ni	

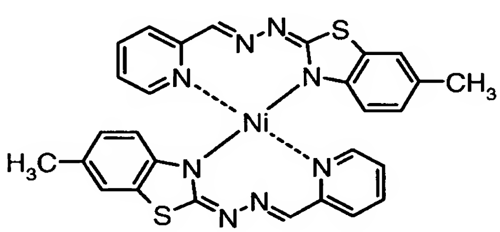
Example	(I)	M	λ_{max}
1r		Co	
1s		Zn	

Example 2

1.1 g of the hydrazone of the formula



were stirred overnight together with 0.47 g of nickel acetate tetrahydrate in 10 ml of methanol at room temperature. The orange suspension was filtered with suction, the solid was washed with methanol and water and dried at 50°C under reduced pressure. This gave 1.12 g (99% of theory) of an orange powder having the formula



Mp. = 248-253°C

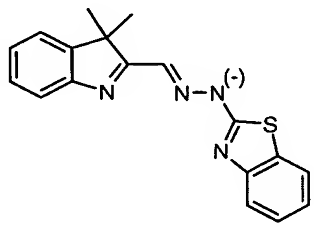
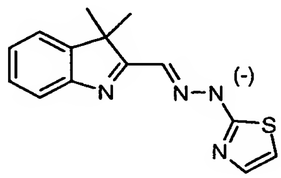
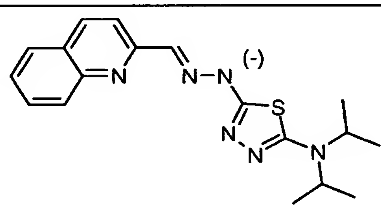
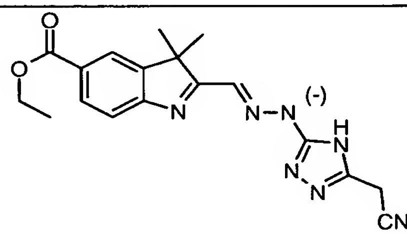
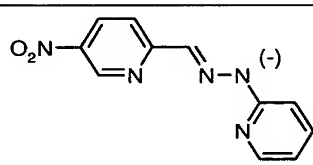
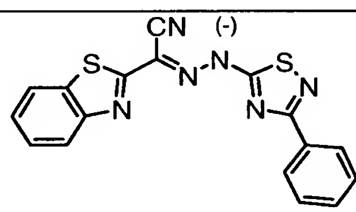
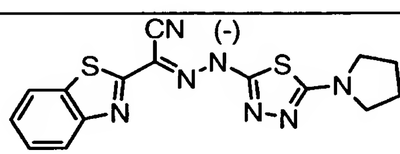
MS: m/e = 592

UV (CH_2Cl_2): λ_{max} = 472 nm.

A 2% strength by weight solution in TFP (2,2,3,3-tetrafluoropropanol) applied to a glass plate gives a glass-like transparent film.

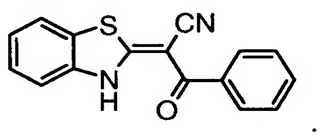
The examples in the following table were also prepared by a method analogous to Example 2.

Table 2

Example	(I)	M	λ_{max}
2a		Ni	
2b		Co	
2c		Ni	
2d		Ni	
2e		Zn	
2f		Ni	483 nm
2g		Ni	526 nm

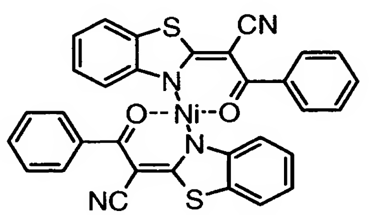
Example 3

a) 2.49 g of 1,1-bis(methylthio)-2-cyano-3-phenyl-1-propen-3-one and 1.25 g of o-aminothiophenol were stirred in 60 ml of ethanol under a nitrogen atmosphere for 6 hours. After cooling, the solid was filtered off with suction, washed with a little ethanol and dried at 50°C under reduced pressure. This gave 2.4 g (86% of theory) of a colourless powder having the formula



Mp. = 238-240°C.

b) 0.7 g of the product from a) were stirred overnight with 0.62 g of nickel acetate tetrahydrate in 6 ml of methanol at room temperature. The solid was filtered off with suction, washed with methanol and dried at 50°C under reduced pressure. This gave 0.65 g (85% of theory) of a greenish yellow powder having the formula

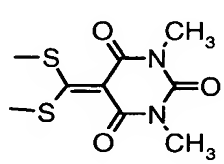


Mp. > 280°C

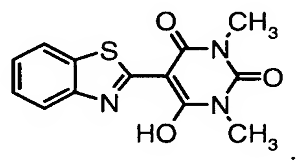
UV (CH_2Cl_2): λ_{max} = 362 nm.

Example 3b

2.6 g of the barbituric acid derivative of the formula



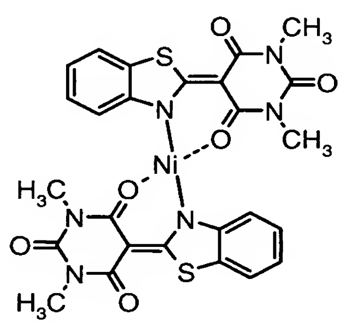
and 1.25 g of o-aminothiophenol were boiled in 40 ml of ethanol under a nitrogen atmosphere for 4.5 hours. The suspension was filtered with suction, the solid was washed with ethanol and dried at 50°C under reduced pressure. This gave 2.6 g (90% of theory) of a yellowish powder having the formula



Mp. > 280°C

λ_{max} = 348 nm in dichloromethane.

b) 0.72 g of the product from a) and 0.62 g of nickel acetate tetrahydrate were stirred overnight in 6 ml of methanol at room temperature. The solid was filtered off with suction, washed with methanol and dried at 50°C under reduced pressure. This gave 0.62 g (78% of theory) of a pale green powder having the formula

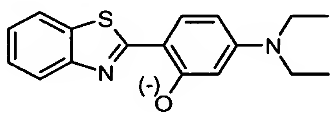
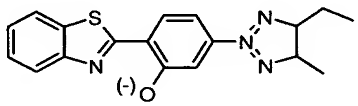
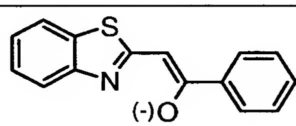
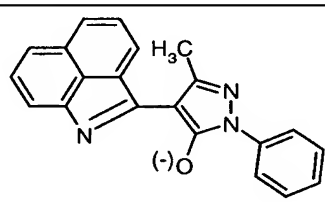
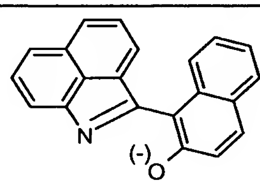
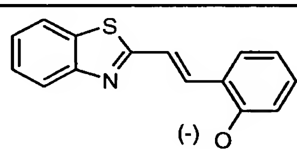
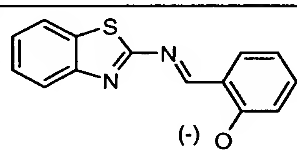


Mp. > 280°C

λ_{max} = 390 nm in dichloromethane.

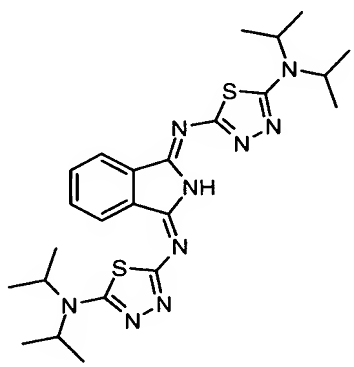
The examples in the following table were also prepared by a method analogous to Example 3.

Table 3

Example	(I)	M	λ_{max}
3a		Ni	
3b		Co	
3c		Zn	
3d		Ni	477 nm
3e		Ni	522, 550 nm
3f		Ni	
3g		Zn	

Example 4

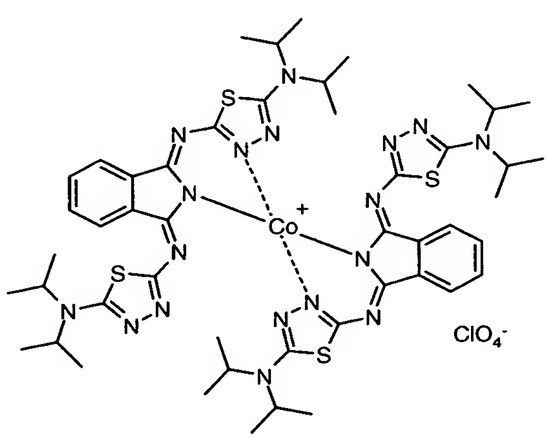
a) 22.9 g of 1-amino-3-iminoisoindole, 63.3 g of 2-amino-5-diisopropylamino-1,3,4-thiadiazole and 3 g of ammonium chloride were stirred under reflux in 200 ml of ethanol for 24 hours. After cooling, the mixture was poured into 300 ml of petroleum ether, filtered with suction, the solid was washed with petroleum ether and water and dried at 50°C under reduced pressure. This gave 58.8 g (73% of theory) of an orange powder having the formula



.

Mp = 192-195°C.

b) 0.13 g of cobalt acetate tetrahydrate together with 20 ml of acetonitrile were placed in a reaction vessel. Three drops of 65% strength by weight nitric acid were added. After 30 minutes, a solution had been formed. 0.27 g of the product from a) was added. After 1 hour at 50°C, the mixture was cooled, diluted with 20 ml of water and precipitated by means of lithium perchlorate. The solid was filtered off with suction, washed with water and dried at 50°C under reduced pressure, giving 0.46 g (78% of theory) of a red powder having the formula



.

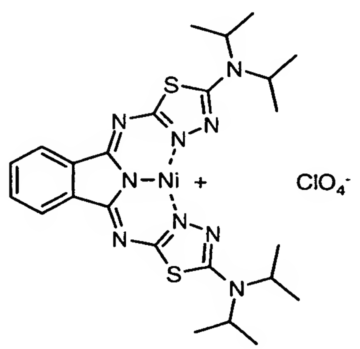
MS: m/e = 1079 (ML_2^+)

UV (CH_2Cl_2): λ_{max} = 453, 501 nm.

A 2% strength by weight solution in TFP (2,2,3,3-tetrafluoropropanol) applied to a glass plate gives a glass-like transparent film.

Example 4a

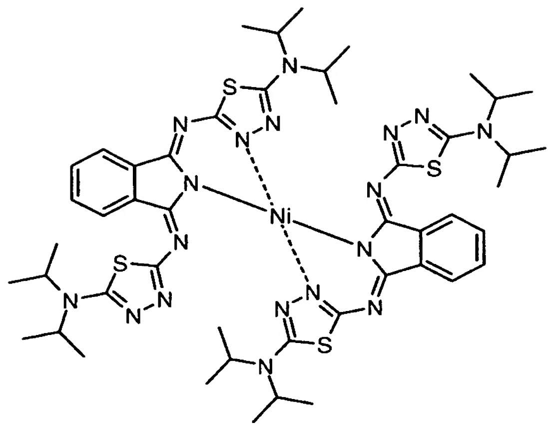
1.3 g of nickel acetate tetrahydrate were dissolved in 30 ml of ethanol. 2.6 g of the product from Example 4, paragraph a), were added. The mixture was stirred at room temperature for 2 hours and then admixed with lithium perchlorate. After stirring for 2 hours, the product was precipitated by addition of water. It was filtered off with suction, washed with water and dried at 50°C under reduced pressure. This gave 2.06 g of an orange powder which was stirred with toluene at room temperature. The insoluble residue was filtered off with suction, washed and dried at 50°C under reduced pressure. This gave 1.09 g of an orange powder of the formula



MS: m/e = 568 (ML^+)
UV (CH_2Cl_2): λ_{max} = 449 nm.

A 2% strength by weight solution in TFP (2,2,3,3-tetrafluoropropanol) applied to a glass plate gives a glass-like transparent film.

1.5 g of a different orange powder having the formula



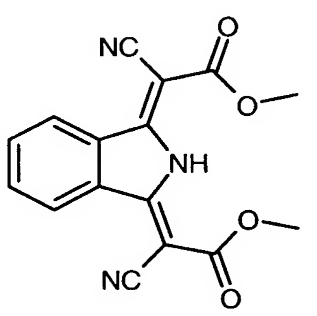
were able to be isolated from the toluene mother liquor by evaporation on a rotary evaporator.

MS: m/e = 1079 (ML_2+H^+)

UV (CH_2Cl_2): λ_{max} = 405, 430, 476, 506, 549 nm.

Example 5

a) 2.18 g of 1,3-diiminoisoindolenine were dissolved in 50 ml of methanol, and a solution of ethyl cyanoacetate in 20 ml of methanol was added dropwise at 20°C. The mixture was stirred for 8 hours at 60°C and subsequently overnight at room temperature. The solid which precipitated was filtered off with suction, washed with a little methanol and dried at 50°C under reduced pressure. This gave 4.52 g (89% of theory) of a yellow powder having the formula

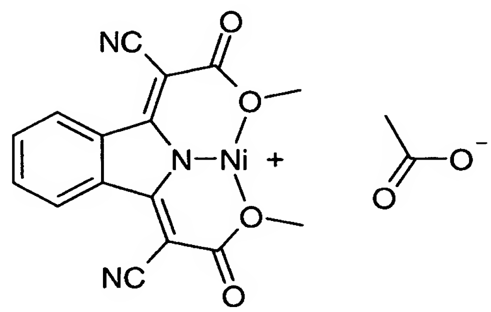


Mp. = 247 - 249°C

UV (acetone): λ_{max} = 393, 416 nm.

b) 0.31 g of the product from a) was stirred with 0.50 g of nickel acetate tetrahydrate in 10 ml of DMF at 100°C for 4 hours. The solution was admixed with 10 ml of water and the solid which

precipitated was filtered off, washed with water and dried at 50°C under reduced pressure. This gave 0.18 g (42% of theory) of a yellow powder having the formula

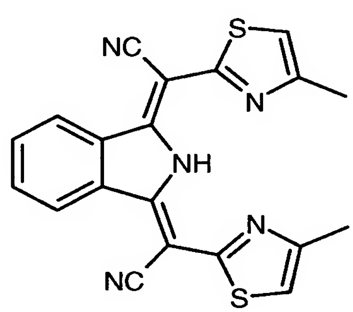


Mp. > 350°C

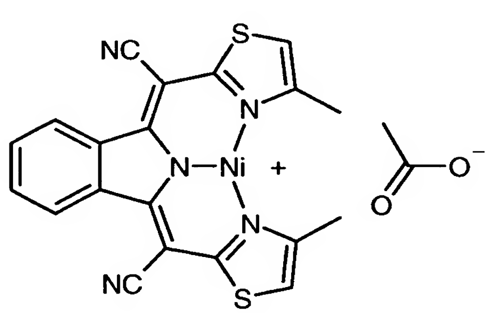
UV (acetone): λ_{max} = 453, 482 nm.

The following examples were prepared analogously.

Example 5a



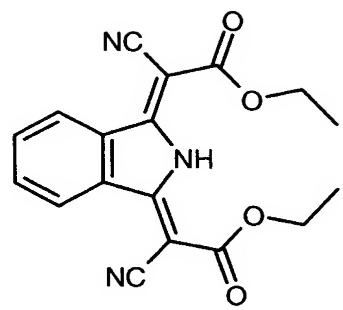
UV (acetone): λ_{max} = 477, 510 nm



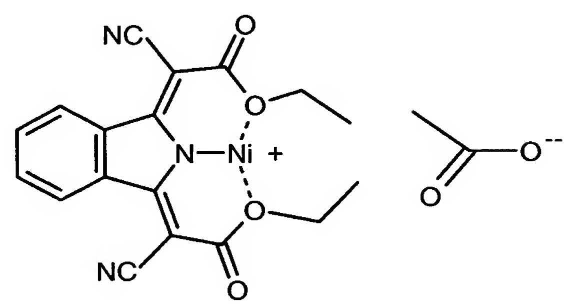
Mp. > 350°C

UV (acetone): λ_{max} = 522, 563 nm

Example 5b



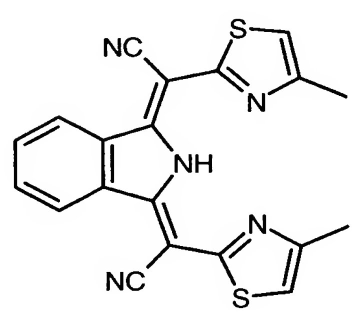
UV (CH_2Cl_2): λ_{max} = 407, 430 nm



Mp. > 350°C

UV (CH_2Cl_2): λ_{max} = 383, 482 nm

Example 5c

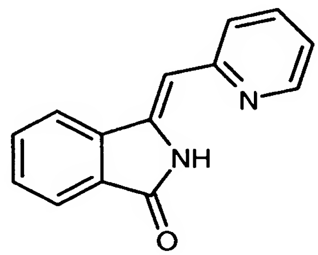


UV (acetone): λ_{max} = 487, 524 nm

Example 6

a) 4.89 g of 2-methylpyridine were dissolved in 5 ml of NMP, and 9.13 g of 3-iminophthalimidine hydrochloride were added a little at a time at 120°C. The solution was stirred at 130°C for another

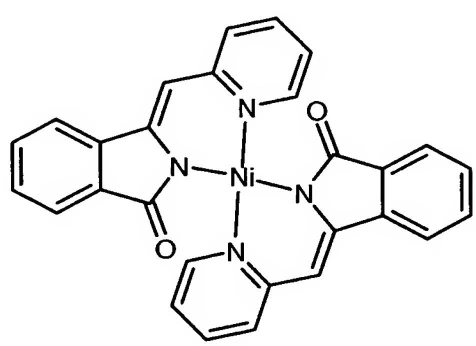
16 hours, stirred into 100 ml of water and the solid which precipitated was filtered off with suction, washed with water and dried at 50°C under reduced pressure. This gave 7.99 g (72% of theory) of a beige-coloured powder having the formula



Mp. = 119 - 121°C

UV (acetone): λ_{max} = 357 nm

b) 0.44 g of the product from a) was stirred with 0.25 g of nickel acetate tetrahydrate in 10 ml of DMF at 100°C for 4 hours. The solid which precipitated was filtered off, washed with ether and dried at 50°C under reduced pressure. This gave 0.32 g (64% of theory) of a greenish powder having the formula

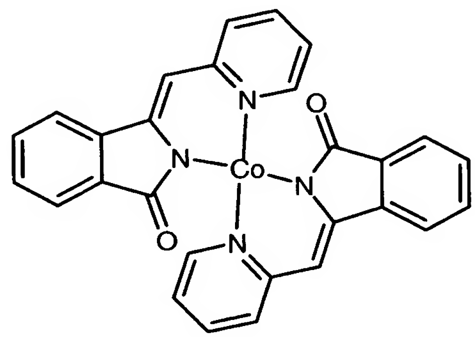


Mp. > 350°C

UV (MeOH): λ_{max} = 392 nm

The following examples were also prepared analogously.

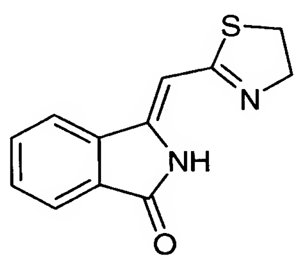
Example 6a



Mp. > 350°C

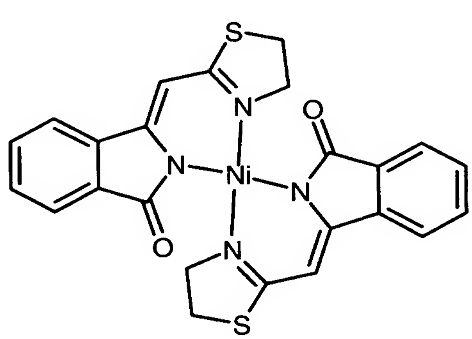
UV (MeOH): λ_{max} = 381 nm

Example 6b



Mp. = 110 - 112°C

UV (CH_2Cl_2): λ_{max} = 336 nm



UV (CH_2Cl_2): λ_{max} = 384 nm

Example 7

A 3% strength by weight solution of the dye from Example 1 in 2,2,3,3-tetrafluoropropanol was prepared at room temperature. This solution was applied by means of spin coating to a pregrooved polycarbonate substrate. The pregrooved polycarbonate substrate had been produced as a disk having a diameter of 12 cm and a thickness of 0.6 mm by means of injection moulding, and the tracking pitch of the groove structure was 740 nm. The disk with the dye layer as information carrier was coated with 100 nm of silver by vapour deposition. A UV-curable acrylic coating composition was subsequently applied by spin coating and a second, identical polycarbonate substrate was placed on top. The acrylic coating composition was homogeneously distributed over the disk surfaces by further spinning and then cured by means of a UV lamp. Writing and reading tests were carried out by means of a dynamic writing test apparatus constructed on an optical test bench comprising a diode laser (λ = 405 nm) for generating linearly polarized light, a polarization-sensitive beam splitter, a $\lambda/4$ plate and a movably suspended collecting lense having a numerical aperture NA = 0.65 (actuator lense). The light reflected by the reflection layer of the disk was taken out from the beam path by means of the abovementioned polarization-sensitive beam splitter and focused by means of an astigmatic lense onto a four-quadrant detector. At a linear velocity V = 3.5 m/s and a writing power P_{write} = 8.5 mW, a signal/noise ratio C/N = 38 dB was measured for 11T pits. The writing power was applied as an oscillating pulse sequence (cf. Figure 3), with the disk being irradiated alternately with the abovementioned writing power P_{write} and the reading power $P_{read} \approx$ 1.9 mW. The writing pulse sequence for the 11T pit comprised a lead pulse having a length T_{top}= 1.5T = 60 *ns*, where T = 40 *ns* is the base time (11T = 440 *ns*). The lead pulse was placed so that it ended after 3T units. It was followed by eight pulses having a length T_{mp} = 30 *ns*, with the time being determined by T_{mp} = 0.75T. A time interval ΔT = 10 *ns* therefore remains free between each writing pulse. The 11T long writing pulse was followed by an 11T long pause. The disk was irradiated with this oscillating pulse sequence until it had rotated once. The marking produced in this way was then read using the reading power P_{read} and the abovementioned signal/noise ratio C/N was measured.

Analogous results were achieved using the metal complexes from the other examples described above.